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Janovsky σ-Complexes

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The methods of preparation, structure, and properties of the coloured products formed in the Janovsky reaction of aromatic polynitro-compounds with acetone and other ketones in an alkaline medium as well as the analogous complexes with other compounds containing mobile hydrogen atoms are examined and the existing ideas about the mechanism of the Janovsky reaction and further transformations of the σ-complexes are discussed.
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I. INTRODUCTION

In 1976 90 years had elapsed since the discovery by the Czech chemist Jaroslav Janovsky of the reaction between *m*-dinitrobenzene and acetone in an alkaline medium. This interaction, which is accompanied by the appearance of a deep colour, has come to be known as the Janovsky colour reaction. It was subsequently extended to various aromatic polynitro-derivatives and ketones. Many investigators have now established that in the majority of cases the colour is due to the formation of σ-complexes—the products of the addition of the nucleophile to the substrate. A number of reviews have been devoted to the structure and properties of anionic σ-complexes [1-6] in which the σ-complexes with acetone and other carbanions are only rarely mentioned. The aim of the present review is to fill the gap in this field. The σ-complexes of aromatic polynitro-compounds with various carbanions can be quite justifiably called "Janovsky σ-complexes". The authors of recently published reviews of the complexes of ketones with polynitro-compounds [7,8] consider mainly the subsequent cyclisation reaction of the Janovsky σ-complexes, which they discovered and investigated (in the present review studies on the structure and properties of the so-called bicyclic complexes are not included).

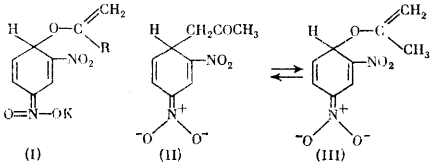
In 1886 Janovsky and Erb [9,10] established that the addition of an alcoholic solution of potassium hydroxide to an acetone solution of *m*-dinitrobenzene (*m*-DNB) causes the appearance of a violet colour. Subsequently, Janovsky [11], Wilgerodt [12], and many other investigators extended this sensitive colour reaction to many ketones and aldehydes [13-19] and also various polynitro-compounds [13,17,20-25]. A series of empirical rules were derived [14,23-25] and it was shown that not only *meta*- but also *ortho*- and *para*-dinitrobenzenes [26] as well as many mononitro-compounds containing an electron-accepting substituent in the *meta*-position with respect to the nitro-group [27,28] tend to undergo the Janovsky reaction.

Apart from alkalis, weak bases such as sodium carbonate or iodide may be used to establish an alkaline medium [29].

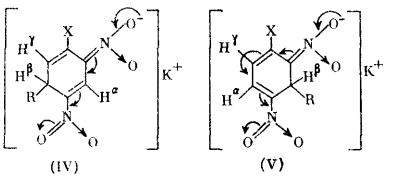
II. INTERACTION OF AROMATIC NITRO-COMPOUNDS WITH ACETONE IN THE PRESENCE OF ALKALI

1. σ-Complexes of *m*-Dinitrobenzene and Its Derivatives

The study of the absorption spectra [23,25,30-36] of solutions of the coloured products of the Janovsky reaction enabled a number of workers [23,25,30] to put forward a hypothesis concerning their structure. Baernstein [30] suggested that the reaction involves the addition of the enolic form of the ketone to the *aci*-form of the nitro-compound with formation of product (I). Canbäck [23,25] believed that real covalent C–C or C–O bonds are not formed in coloured products of types (II) and (III) and that the linkage between *m*-DNB and the acetone residue is one between a dipole and an anion. Subsequently evidence was adduced in support of both the enolic form (III) [21,22,28,36] and the keto-form (II) [14,37,38].



(I) (II) (III)



(IV) (V)

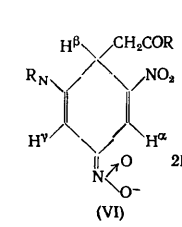
The first convincing evidence concerning the formation in the Janovsky reaction of isomeric complexes (IV) and (V), differing in the site of addition of the acetone residue, was presented by Gitis and coworkers [39-41]. Having observed the absence of a colour in the case of 2,4-dinitromesitylene, they investigated a large number of model compounds in which the substituent X prevents the addition

of the acetone residue R to the carbon atom linked to the substituent. When the 3- and 5-positions in the molecule of a 1-X-2,4-dinitro-compound are vacant, both complexes, (IV) and (V), are formed in all cases and the absorption spectra show two maxima. If the 3-position is occupied by a substituent, complex (IV) is formed and the spectrum shows only the short-wavelength absorption maximum (λmax = 550–570 nm). The introduction of a substituent into the 5-position leads to the formation of complex (V) only, which gives rise to the long-wavelength absorption maximum (λmax = 600–690 nm). This product is less stable and cannot be detected for certain *m*-DNB derivatives containing an electron-donating substituent X.

The conclusions reached about the structure of the coloured Janovsky complexes[39,40] were confirmed by studies of the influence of substituents on the positions of both absorption maxima (Table 1) using correlation analysis[41–43]. Analogous conclusions concerning the correspondence of the absorption maxima to definite coloured reaction products were arrived at somewhat later by Pollitt and Saunders[43,44], who believe[43] that the hypsochromic shift of the two absorption maxima, caused by the majority of substituents, is due to the displacement of the nitro-groups from the plane of the ring. According to their view[44], direct attack by the HO^- ion on the polynitro-compound is possible together with the formation of Janovsky complexes in dimethylformamide and the assignment of the bands in the absorption spectra is difficult, particularly for electronegative substituents.

Thus, using model compounds, various investigators came close to the determination of the structure of the products of the above reaction with the aid of electronic absorption spectra. The final answers to a number of questions concerning the detailed structure of the coloured complexes were obtained as a result of their isolation in a free form and their investigation by ^{1}H NMR and infrared spectroscopy.

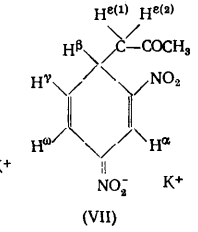
The first attempts[14,15,36,38] to isolate these products were unsuccessful—in all cases the decomposition products of the Janovsky complexes and not the complexes themselves were obtained. The first successful synthesis of this kind was achieved by Akatsuka, who was able to obtain the dark-violet products of the addition of acetone and acetophenone to 3,5-dinitrobenzenesulphonic acid[45] and 3,5-dinitrobenzoic acid[46] in the presence of K_2CO_3. The reaction products were identified by elemental analysis, paper chromatography, and their conversion into *S*-benzylthiuronium salts[47], which made it possible to attribute to them structure (VI):



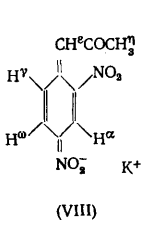
(VI)

$R_N = SO_3^-$ or COO^-

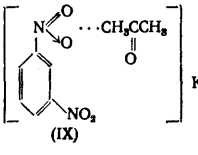
R=CH_3 (a) or C_6H_5 (b)



(VII)



(VIII)



(IX)

Table 1. The electronic spectra of Janovsky σ-complexes obtained from *m*-DNB derivatives in acetone.

X	λ_1, nm	lg ε_1	λ_2, nm	lg ε_2	λ_1, nm	lg ε_1	λ_2, nm	lg ε_2	Refs.
Isomeric σ-complexes of 1-X-2,4-dinitrobenzenes	(IV)				(V)				
H	572	4.28	—	—	689, 692	—	—	—	51, 39, 44
H[a]	555	4.03	—	—	—	—	—	—	56
H[b]	587	4.29	—	—	—	—	—	—	51, 56
H[c]	582	3.75	—	—	—	—	—	—	51, 56
CH_3	573	4.28	335	4,079	670, 662	—	—	—	60, 39, 65
CH_3	563, 580	4.15	—	—	665	—	—	—	65, 68, 44
C_2H_5	568, 565	4.19	—	—	670	—	—	—	23, 63
$CH(CH_3)_2$	567	4.26	—	—	678	—	—	—	63, 65
$C(CH_3)_3$	564	4.08	—	—	680	—	—	—	63, 65
CH_2COO^-	576	3.88	—	—	—	—	—	—	23
CH_2COOCH_3	579	4.05	—	—	—	—	—	—	23
OCH_3	562, 550	4.35	354	4,079	625, 626	4.32	338	4.54	60, 65, 40
OC_2H_5	561	—	—	—	626	—	—	—	40
OC_6H_5	571, 561	—	—	—	638	—	—	—	40, 23
OCF_3	545	—	—	—	647	—	—	—	40
F	570, 562	—	—	—	641, 633	—	—	—	44, 40
Cl	545, 561	4.34	376	—	668, 665	—	360	—	23, 82
Cl	548	—	—	—	666, 660	—	—	—	44, 40
Br	545, 560	—	—	—	663, 675	—	—	—	40, 23, 44
I	550	—	—	—	672	—	—	—	40
CN	548	—	—	—	705	—	—	—	44
CN[c]	551	—	370	—	—	—	—	—	44
$COOCH_3$[c]	552	—	358	—	—	—	—	—	44
$COOCH_3$	560, 567	4.42	376	4,009	686, 685	4.25	357	4.62	60, 23, 44
$COOCH_3$[d]	558	4.45	372	4,065	686	4.26	354	4.61	60
SC_2H_5	578	4.52	396	4,350	568	4.48	362	4.45	60
SCN	560	4.36	380	4,190	660	4.21	342	4.27	60
NH_2[e]	522, 525	4.12	385	—	—	—	—	—	40, 65
NH_2[e]	529	—	398	—	—	—	—	—	44
$NHNH_2$	568, 570	3.62	—	—	—	—	—	—	23, 40
$NHCOCH_3$[e]	425	4.35	—	—	—	—	—	—	23
Isomeric σ-complexes of 1-X-3,5-dinitrobenzenes	(XI)				(X)				
CH_3	584, 580	4.52	360	4,24	—	—	—	—	60, 44
CH_3[c]	588	—	360 & 372[f]	—	—	—	—	—	44
OCH_3	590	4.35	360	4,24	—	—	—	—	44, 60
OCH_3[c]	603	—	360 & 372[f]	—	—	—	—	—	44
Cl	563	—	—	—	—	—	—	—	44
Cl[c]	570	—	365	—	726	—	379	—	44
CN	549, 530	4.10	396	—	631	—	—	—	44, 58
CF_3	533	4,40	373	—	639	4.26	373	—	60
COO^-	568, 563	—	380	—	660	—	—	—	44, 23
COO^-[c]	580	—	406	—	640	—	—	—	44
COOCHg	547	4,15	417	4,15	560	—	410	—	62
$COOCH_3$	561	—	—	—	625	—	406	—	44
$COOCH_3$[b]	545, 572	—	414	—	630	—	407	—	59, 44
$COOC_2H_5$	558	4.48	424	4,39	628	4 41	408	4.62	60
	563	—	—	—	625	—	406	—	44
$CONH_2$	580	—	—	—	640	—	403	—	44
$CONH_2$	580	—	404	—	650	—	—	—	44
$CON(CH_3)_2$	553	4,23	385	4,04	—	—	—	—	62
Isomeric σ-complexes of 1-X-3,5-dinitrobenzenes	(XI)				(X)				
$CON(C_2H_5)_2$	582	—	399	—	656	—	—	—	44
CON⟨H⟩	560	4.11	385	3.78	655	4.00	407	3.90	62
SO_3OCH_3	555	2.88	—	—	—	—	—	—	45–47
$SO_3OC_6H_5$	555	3.92	—	—	—	—	—	—	45–47
NH_2	—	—	—	—	624	—	—	—	44
$N(CH_3)_2$	—	—	—	—	614	—	—	—	44
$N(CH_3)_2$[c]	—	—	—	—	625	—	377	—	44

a) Ethanol (lg ε = 4.076 in tetrahydrofuran); *b*) DMSO; *c*) DMF; *d*) $(n\text{-}C_4H_9)_4\overset{+}{N}$ cation; *e*) it has been shown[40,44] that the formation of a colour in the presence of these substituents is due to the elimination of a hydrogen atom from the amino-group and the formation of the 2,4-dinitrophenylanilinium ion; *f*) double maximum; *g*) acetone + 10% of methanol.

Gitis and Kaminskii[48] developed a spectrophotometrically monitored synthesis of classical Janovsky complexes from *m*-DNB, 1,3,5-trinitrobenzene (TNB), and then 2,4-dinitroanisole[49]. It was established[48,50] that they are σ-complexes of type (VII), where the acetone residue adds in

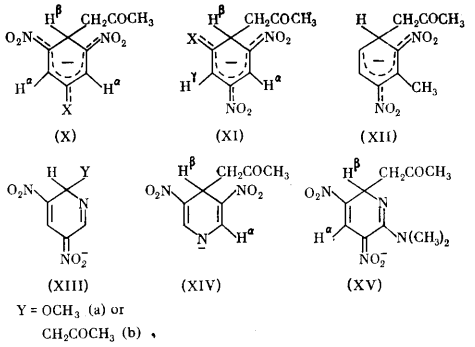
the keto-form to a ring carbon atom with formation of a covalent C–C bond. This is confirmed by the presence in the infrared spectra of the ν(C=O) band at 1710 cm^{-1}, whose position and intensity are close to those of the ν(C=O) band of 2,4-dinitrophenylacetone. Furthermore, a small amount of 2,4-dinitrophenylacetone was detected together with the initial *m*-DNB in the products of the acid decomposition of complex (VII).[50] By treating an acetone solution of *m*-DNB with solid KOH, Kimura et al.[51] also isolated the Janovsky complex (VII), whose structure was demonstrated by elemental analysis and by comparison with the specially prepared potassium salt of 2,4-dinitrophenylacetone (VIII).

Contrary to generally accepted ideas, Ryzhova and coworkers[52-54] suggest that the products of the interaction of *m*-, *o*-, and *p*-dinitrobenzenes, which they obtained in the presence of KOH by reaction with acetone, acetophenone, cyclohexane (cyclohexanone?), and ethyl methyl ketone and which have the 1 : 1 and 1 : 2 compositions, are donor–acceptor complexes of type (IX), formed as a result of the local interaction of the ketone with the nitro-group. However, the evidence presented by these workers[54] in support of structure (IX) cannot be regarded as convincing; it conflicts with all the available data concerning the structure of Janovsky complexes.

The ^{1}H NMR spectrum of a Janovsky σ-complex of *m*-DNB was studied for the first time by Fyfe and Foster[55], who obtained this complex by adding solid sodium methoxide to a solution of *m*-DNB in a 1 : 1 mixture of acetone and dimethyl sulphoxide (DMSO). The structure of the σ-complex (VII) was confirmed by its characteristic chemical shifts and spin–spin coupling constants: δ = 8.32 (H^{α}), 4.17 (H^{β}), 5.38 (H^{γ}), and 6.6 p.p.m. (H^{ω}); $J_{\alpha,\omega}$ = 1.9 and $J_{\gamma,\omega}$ = 10.2 Hz. The $H^{\epsilon(1)}$ and $H^{\epsilon(2)}$ methylene protons are non-equivalent owing to the lack of symmetry of the $C_{(1)}$ atom. As a result of the spin–spin coupling with H^{γ}, $H^{\epsilon(1)}$ and $H^{\epsilon(2)}$, the signal due to the H^{β} nucleus is therefore a quintet; $J_{\beta,\gamma} = J_{\beta,\epsilon(1)}$ = 5.0 and $J_{\beta,\epsilon(2)}$ = 10.0 Hz. This assignment of the signals is confirmed by the ^{1}H NMR spectrum of the analogous complex obtained from hexadeuteroacetone. In the reaction solutions investigated no isomers of type (V, X = H) were detected. The σ-complex (VII) was isolated in a free form[56] by treating an acetone solution of *m*-DNB with potassium hydroxide and subsequent precipitation with benzene. The infrared spectrum of the complex showed absorption bands at 1719 cm^{-1} (C=O), 1290 cm^{-1} ($sym.NO_2^-$), and 1610 cm^{-1} (C=C).

The electrochemical reduction of the σ-complex (VII) at the potential of the first reversible reduction wave (~ 1.0 V) in acetone in the presence of $(n\text{-}Bu)_4NClO_4$ as the supporting electrolyte made it possible to obtain for the first time[57] its radical-dianion, which was detected by ESR. The large difference between the splittings due to the ^{14}N nuclei confirms the non-equivalence of the nitro-groups and the quinonoid structure of the complex.

The structure and properties of the σ-complexes of acetone with various *m*-DNB derivatives have been studied in detail by ^{1}H NMR and infrared spectroscopy. Initially these complexes were investigated in reaction solutions and then most of them were isolated in a free form. Thus Foreman and Foster[58] showed that, when acetone solutions of 1-X-3,5-dinitrobenzenes (X = COOMe and COO^-) are treated with triethylamine or sodium methoxide, the σ-complex (X) is formed initially, but after several days is converted into a 7 : 1 equilibrium mixture of isomers (X) and (XI):



This is consistent with the results obtained for X = CF_3 and CN.[59] The exchange interaction of σ-complexes containing other substituents with the free radicals formed in the reaction mixture leads to a broadening of the signal and, when diethylamine is used[59], the exchange altogether precludes the measurement of the ^{1}H NMR spectrum.

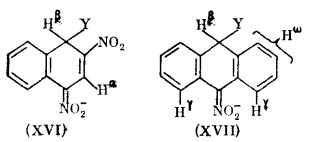
Such broadening does not occur in the study of the ^{1}H NMR spectra of complexes isolated in a free form. Because of this, Gitis and coworkers were able to investigate a large number of σ-complexes of *m*-DNB derivatives, obtained by the spectrophotometrically monitored synthesis which they developed previously[48]. Analysis of the electronic, ^{1}H NMR, and infrared spectra of the σ-complexes of a series of 1-X-3,5-dinitrobenzenes (X = Me, OMe, COOEt, or CF_3 [60,61] and X = COOMe, $CONC_5H_{10}$, $CONMe_2$, or $CONH_2$ [62]) also confirmed (Table 2) that they are a mixture of isomers (X) and (XI), with the latter predominating; the stability of the complexes increases with enhancement of the electron-accepting properties of the substituent. The σ-complexes of a series of 1-alkyl-2,4-dinitrobenzenes[63-65] (alkyl = Me, Et, iso-Pr, or t-Bu) and a series of 1-X-2,4-dinitrobenzenes[60,65] (X = OMe, COOMe, SEt, or SCN) were obtained by a similar procedure. In the latter case the formation of two isomeric complexes of types (IV) and (V), differing in the site of addition of the acetone residue (R = CH_2COCH_3), established previously on the basis of electronic absorption spectra[39,40], was finally demonstrated with the aid of ^{1}H NMR and infrared spectra. Complex (IV) is more stable owing to the presence in the *para*-position with respect to the rehybridised carbon atom of a powerful electron acceptor (the nitro-group). The type (V) isomer with X = OMe is extremely unstable and, when X = H or alkyl, it cannot be obtained in a free form at all. Enhancement of the electron-accepting properties of the substituent increases the stability of this complex; for X = COOMe, it was isolated[60] in a mixture with isomer (IV). It is noteworthy that, for sulphur-containing substituents (X = SCN or SEt), the opposite behaviour is observed: isomer (V) becomes more stable than isomer (IV).

It has recently been possible to isolate in a free form[66] extremely labile σ-complexes of 1-halogeno-2,4-dinitrobenzenes (halogen = F, Cl, Br, or I), which, according to ^{1}H NMR, infrared, and electronic spectroscopic data, are also mixtures of isomers of types (V) and (IV) with the latter predominating (with the exception of the fluorine-containing complex). The synthesis of a series of σ-complexes from *m*-DNB derivatives showed that the spectra contain new maxima in the near ultraviolet in addition to the absorption maxima in the visible region known previously[40-42] (Table 1). On the basis of the successful[67]

chromatographic separation of isomers (X) and (XI) with X = COOEt and the resolution of the overlapping bands into their components, the short-wavelength maximum in the ultraviolet region was assigned to isomers of type (V) (λ_{max} between 338 and 350 nm for different substituents X) and type (X) (λ_{max} = 360–408 nm), while the long-wavelength maximum was assigned to isomers of type (IV) (λ_{max} = 354–396 nm) and type (XI) (λ_{max} = 360–424 nm) (Table 1). The resolution of the bands using the characteristics of the complexes isolated made it possible to observe[68] in the spectra of the reaction solutions an absorption maximum for 2,4-dinitroanisole (λ_{max} = 625 nm) corresponding to the unstable isomer (V, X = OMe) and a maximum at 515 nm for 2,6-dinitrotoluene corresponding to a product of the transformation of the σ-complex (XII).

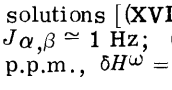
A number of studies[58–68] showed that the presence of electron-accepting groups in the molecule of the *m*-DNB derivative increases the stability and hence the yield of the σ-complexes formed. Both isomers of the σ-complexes derived from 1-X-3,5-dinitrobenzenes, (X) and (XI), are much more stable than the corresponding isomers (V) and (IV) obtained from 1-X-2,4-dinitrobenzenes. The σ-complexes of 3,5-dinitropyridine with acetone[69], formed as a mixture of isomers (XIIIb) and (XIV) with the latter predominating (λ_{max} = 519 nm) following the addition of acetone to a solution of the alkoxide complex (XIIIa) in DMSO, are still more stable. On the other hand, solvolysis by acetone of the methoxide complex of 2-dimethylamino-3,5-dinitropyridine results in the formation[69] of a single acetone σ-complex, probably having structure (XV), with characteristic signals at δ = 8.14 and 5.1 p.p.m. for H^{α} and H^{β} respectively[69].

Stabilisation of the same type owing to the electron-accepting properties of condensed aromatic rings enabled Foster and coworkers[70] to obtain fairly readily the σ-complexes of 1,3-dinitronaphthalene (XVIa) and 9-nitroanthracene (XVIIa) by treating their acetone solutions with triethylamine. The structures of these σ-complexes were demonstrated on the basis of the ^{1}H NMR spectra of their solutions [(XVIa): δH^{α} = 8.76 p.p.m., δH^{β} = 4.81 p.p.m., $J_{\alpha,\beta} \simeq 1$ Hz; (XVIIa): $\delta H\beta$ = 4.29 p.p.m., δH^{γ} = 8.72 p.p.m., δH^{ω} = 7.16 p.p.m.].



When acetone solutions of 4′-substituted α-cyano-4-nitrostilbenes (R = NO_2 or Me) were treated with sodium methoxide, the corresponding σ-complexes (XVIII) were obtained[71]. The observed absorption maxima (λ_1 = 543 nm, λ_2 = 576 nm) correspond to products of the addition of the acetone residue to the double bond (XVIIIa), which in the authors view are formed from the alkoxide addition products (XVIIIb). The ^{1}H NMR spectra of the reaction solutions indicate the presence of a single adduct of type (XVIII) regardless of the *cis*- or *trans*-structure of the initial 4-nitrostilbene.

Table 2. ^{1}H NMR spectra of the Janovsky σ-complexes obtained from *m*-DNB and its derivatives (R = CH_2COCH_3) in [D_6] dimethyl sulphoxide.

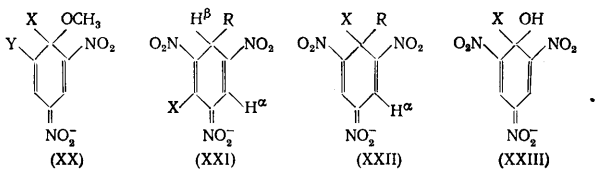
X	Isomer	δ H^{α} (doublet)	δ H^{β} (triplet)	δ H^{γ} (doublet)	$J_{\alpha,\beta}$	$J_{\alpha,\gamma}$	$J_{\beta,\gamma}$	Refs.
From 1-X-2,4-dinitrobenzenes[a]								
H[b]	(VII)[b]	8.32	4.17	5.38	0.6	—	5.0	55
H	(VII)[d]	8.26	4.17	5.36	—	—	4.5	56, 131
CH_3	(IV)	8.40	3.93	5.45	—	—	6.6	63, 65
C_2H_5	(IV)	8.41	4.04	5.12	—	—	6.0	63
$CH(CH_3)_2$	(IV)	8.45	4.05	5.20	—	—	6.0	63, 65
$C(CH_3)_3$	(V)	8.39	4.05	5.07	—	—	5.6	63, 65
OCH_3	(IV)	8.33	4.09	4.46	0.8—1.5	—	5.8	60, 65
	(V)	7.42	5.07	5.07	0.8—1.5	8.5	—	60, 65
F	(IV)	8.31	4.18	4.89	—	—	5.7	66
	(V)	7.47	5.17	4.95	—	8.5	—	66
Cl	(IV)	8.45	4.09	5.75	—	—	6.5	66
	(V)	7.08	5.50	5.43	—	8.0	—	66
Br	(IV)	8.42	4.09	5.75	—	—	6.5	66
	(V)	7.08	5.50	5.43	—	8.0	—	66
I	(IV)	8.38	3.98	6.12	—	—	—	66
	(V)	7.00	5.91	5.65	—	7.7	—	66
$COOCH_3$[e]	(IV)	8.21	4.14	5.50	0.8—1.5	—	5.5	60, 65
	(V)	7.43	5.08	5.06	0.8—1.5	7.6	—	60, 65
SC_2H_5	(IV)	8.36	4.16(m)	4.91	0.8—1.5	—	5.8	60, 65
	(V)	7.32	5.14	5.25	0.8—1.5	8.3	—	60, 65
SCN	(IV)	8.21	4.25	5.64	0.8—1.5	—	5.8	60, 65
	(V)	7.49	5.08	5.60	0.8—1.5	7.8	—	60, 65
OCH_3[f]	(IV)	8.43	4.13	4.52	—	—	—	137
	(V)	7.56	5.01	5.10	—	—	—	137
From 1-X-3,5-dinitrobenzenes[g]								
CH_3	(XI)[h]	8.35	4.14	6.47	0.8	2.0	2.0	60, 61
OCH_3	(XI)[h]	8.20	4.21	5.83	1.5	1.6	—	60, 61
CN	(XI)[d]	8.05	4.24	7.17	0.8	2.0	—	58
	(X)[d]	7.40	4.91	—	0.8	2.0	—	58
CF_3	(XI)[h]	8.37	4.54	7.32	1.0	2.0	2.0	60, 61
	(XI)[d]	7.95	4.29	7.00	—	2.0	—	58
	(X)[h]	7.64	5.18	—	0.5	—	0.5	61, 67
	(X)[d]	7.32	4.91	—	—	—	—	58
COOH	(XI)[d]	8.35	4.68	7.58	1.0	2.0	—	59
	(X)[d]	8.23	5.10	—	1.0	—	—	59
$COOCH_3$	(XI)	8.27	4.61	7.80	1.0	1.9	—	62
	(XI)[d]	8.31	4.61	7.82	1.0	2.0	—	59
	(X)	8.02	5.06	—	0.8	—	—	62
	(X)[d]	7.87	6.22	—	1.2	—	—	59
$COOC_2H_5$	(XI)[h,i]	8.36	4.65	7.87	1.1	2.0		60, 61
	(X)[h,i]	8.09	5.09	—	0.8	—	0.8	60, 61
$CON(CH_3)_2$	(XI)	8.29	4.63	6.80	1.0	1.7	—	62
	(X)	7.75	5.09	—	0.7	—	—	62
	(XI)	8.25	4.56	6.73	0.8	1.8	—	62
	(X)	7.69	5.07	—	1.0	—		62
CN[j]	(XI)	8.18	4.33	7.35	—	2.0	—	59
	(X)	7.55	4.50	—	—	—	—	59
CN[k,l]	(XI)	8.29	4.82	7.42	—	1.9	0	111
	(X)	7.55	5.40	7.64	—	—	—	111
$COOCH_3$[k,m]	(XI)	8.29	4.82	7.72	1.2	1.8	—	111
	(X)	7.96	5.29	8.04	1.0	1.0	—	111
$CONC_5H_{10}$[k,n]	(XI)	8.26	4.78	6.66	1.0	2.0	—	111

a) usually δ(CH_2) = 3.10–3.20 p.p.m., δ(CH_3) = 2.05–2.15 p.p.m., and $J_{\beta CH_2} \simeq 5.0$ Hz for the added acetone residue; *b*) δH^{ω} = 6.57 p.p.m., $J_{\alpha,\omega}$ = 1.9 Hz, $J_{\gamma,\omega}$ = 10.2 Hz, and $J_{\beta,\omega}$ = 1.0 Hz; *c*) in a 1 : 1 acetone–DMSO mixture; *d*) in DMSO; *e*) all the signals are the same for the (n-C_4H_9)$\overset{+}{N}$ K^+ cations; *f*) complexes with acetonitrile (R = CH_2CN), $\lambda_{max}(CH_3CN)$ = 590 nm (IV) and 618 nm (V); *g*) δ(CH_2) = 2.37–2.50 p.p.m., δ(CH_3) = 2.02–2.14 p.p.m., J_{β,CH_2} = 6.0–4.0 Hz (XI), and J_{β,CH_2} = 5.6–5.0 Hz (X) for the added acetone residue; *h*) in [D_6] acetone; *i*) signals due to the C_2H_5 group in isomers [δ(CH_2) = 4.13 p.p.m. and δ(CH_3) = 1.21 p.p.m. for (XI); δ(CH_2) = 4.11 p.p.m. and δ(CH_3) = 1.19 p.p.m. for (X)]; *j*) complex with $C_2H_5COC_2H_5$, J_{β,CH_2} = 4.0 Hz; *k*) complexes with cyclohexanone; *l*) J_{β,CH_2} = 1.5 Hz (XI) and 7.0 Hz (X), λ_{max} = 640 nm (X) and 540 nm (XI); *m*) J_{β,CH_2} = 6.5–6.0 Hz, λ_{max} = 625 nm (X); *n*) J_{β,CH_2} = 2.0 Hz, λ_{max} = 550 nm.

The formation of Janovsky σ-complexes from mononitrobenzenes was demonstrated by Reutov and coworkers[72] who obtained a solution of the σ-complex (XIX) (λ_{max} = 490 nm; $\lg\epsilon \simeq 4.25$) by adding an alcoholic solution of KOH to an acetone solution of *m*-nitrophenyldiphenylsulphonium fluoroborate. Its structure was demonstrated with the aid of ^{1}H NMR spectra (δH^{β} = 5.80 p.p.m., δH_{Ar} = 8.0–7.4 p.p.m.) and also by synthesising the same product by the reaction of the initial substrate with $CH_3COCH_2.HgCl$ in the presence of Bu_4NI.

2. Janovsky σ-Complexes of 1,3,5-Trinitrobenzene and Its Derivatives

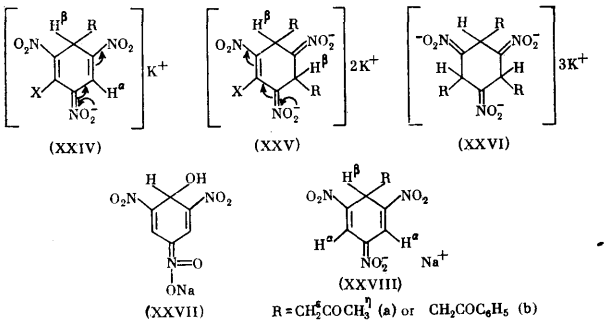
In studies of the structure of the coloured products of the interaction of *sym*-TNB and its derivatives with acetone in an alkaline medium many workers compared their absorption spectra with those of Meisenheimer σ-complexes, for which a structure of type (XX, Y = NO_2, X = OMe) was regarded as generally accepted[1–6]:



(XX) (XXI) (XXII) (XXIII)

Thus Kimura[73] suggested that the bands observed for 1-X-2,4,6-trinitrobenzenes in an acetone–methanol mixture in the presence of alkali (λ_1 = 450 nm and λ_2 = 520–530 nm) are due to the products (XXI)–(XXIII) (R is the acetone residue). When X = H, Cl, Me, OMe, OEt, or NEt_2, structure (XXI) is characteristic of the complexes and, when X = OPh, COOH, or COOEt, the latter has structure (XXII). Having established the similarity of the absorption spectra of picryl chloride[74,75] and tetryl in water, methanol, and acetone in the presence of alkali, Abe concluded[75–77] that in both cases the colour is due to product [XXIII, X = Cl or N(NO_2)Me]. Pollitt and Saunders[44] suggested that, of the three bands (462, 570, and 518 nm) observed for *sym*-TNB, the first two correspond to a 1 : 1 complex and the third is due to side products. Spectroscopic determination of the composition of the complex of 2,4,6-trinitrobenzoic acid (TH) with acetone (HA) (1 : 2) enabled Neufer et al.[78] to ascribe to it the structure $TH.A^- + H_2A^+$.

Detailed spectrophotometric studies[39,79] showed that, of the three structures (XXIV), (XXV), and (XXVI) proposed[39] for the products derived from *sym*-TNB, only one is actually formed, namely (XXIV, X = H). It is fairly stable and has two maxima in the visible region (at 462 and 568 nm) with an intensity ratio of 2 : 1. On the other hand, in the presence of a large excess of alkali[80] additional maxima appear at 430 and 518 nm, corresponding to the formation of the product of the addition of a hydroxide ion to a molecule of the trinitro-derivative (XXIII, X = H). When potassium methoxide is used as the alkaline agent, the complex (XX, X = H, Y = NO_2) is formed together with (XXI, X = H).



(XXIV) (XXV) (XXVI)

(XXVII) (XXVIII)

R = $CH_2^{\epsilon}COCH_3^{\eta}$ (a) or $CH_2COC_6H_5$ (b)

Owing to the greater stability of the σ-complexes obtained from *sym*-TNB compared with the complexes of *m*-DNB, studies on their synthesis have been more successful. Thus, by allowing an acetone solution of *sym*-TNB to react with NaOH, Giua[81] isolated a red-brown crystalline product. The author believed that in this case an NaOH molecule adds on and the compound has the structure (XXVII). However, the data available at present suggest that in reality he isolated for the first time the Janovsky σ-complex of *sym*-TNB (XXVIIIa). By allowing solid sodium bicarbonate to react with an acetone solution of *sym*-TNB, Kimura[82] obtained a σ-complex, to which he attributed the structure (XXVIIIa) on the basis of analysis and determination of the molecular weight. He obtained the analogous acetophenone complex (XXVIIIb) from an alcoholic solution[51]. By carrying out the reaction in an indifferent solvent, Gitis[26] obtained products of the addition of two and three molecules of the sodium derivative of acetone to di- and tri-nitro-compounds in the form of amorphous brown powders, which are rapidly converted into a tar in air. By treating acetone solutions of *sym*-TNB and some of its derivatives with concentrated aqueous ammonia and subsequently evaporating the solvent *in vacuo*, Abe[75] isolated dark-red crystalline substances and suggested that they are products of the addition of ammonium hydroxide to polynitro-compounds (XXIII). A stable σ-complex of *sym*-TNB with acetone was isolated as a result of a spectrophotometrically monitored synthesis[48]; it was shown[48,50] that it has the structure (XXVIIIa), in which the acetone residue in the keto-form is attached to a ring carbon atom.

Foster and Fyfe[83] established that, when the methoxide complex of *sym*-TNB (XX, X = H, Y = NO_2) is dissolved in acetone, the methoxy-group is replaced by the conjugate base of the solvent with formation of the corresponding Janovsky complex (XXVIIIa). The signal of the H^{β} proton in its ^{1}H NMR spectrum at 5.18 p.p.m. is split into a triplet (J = 9 Hz) owing to the interaction with neighbouring methylene protons; the signal due to the ring protons H^{α} at 8.47 p.p.m. consists of a doublet (J = 1 Hz). A similar substitution occurs when an acetone solution of *sym*-TNB is acted upon by sodium methoxide. If the substitution is carried out in hexadeuteroacetone, a broad unresolved band at 5.18 p.p.m. is observed for H^{β}, which indicates the formation of the σ-complex (XXVIII, R = CD_2COCD_3). When trimethyl- or triethyl-amine was added to an acetone solution of *sym*-TNB, the σ-complex (XXVIIIa) was isolated in a free state[84]. This made it possible to assign the signals of the attached acetone residue (δH^{ϵ} = 2.65 p.p.m., J = 5 Hz; δH^{η} = 2.15 p.p.m.) and the cation H^+NMe_3 (δ = 2.85 p.p.m.) in the ^{1}H NMR spectra. The positions of the signals in the ^{1}H NMR spectrum and of the absorption maxima in the electronic spectra (λ_1 = 557–572 nm and λ_2 = 460–465 nm) as well as their intensities change somewhat as a function of the nature of the cation (Table 3). Similarly

the interaction of *sym*-TNB with diethylamine and other secondary amines[85] leads to the formation of σ-complexes of type (XXVIII) with the $H_2\overset{+}{N}R_2$ cation. However, the authors showed that in this case the reaction is accompanied by the formation of a whole series of side and intermediate products.

In the reaction of the organomercury derivatives of acetone $(CH_3COCH_2)_2Hg$ and $CH_3COCH_2.HgX$ with *sym*-TNB in the presence of NaI in DMSO Beletskaya et al.[86] detected by ^1H NMR the formation of the σ-complex (XXVIIIa) in a high yield via the mechanism

$$CH_3COCH_2HgX + \textit{sym}\text{-TNB} + 2NaI \rightarrow (XXVIIIa) + HgIX \cdot NaI \quad (1)$$

The resulting complex is stable in solution for a long time and its ^1H NMR spectra agree with those described in the literature[83,84]. The σ-complex (XXVIIIa) was obtained by a similar procedure as a result of the interaction of the organotin derivative of acetone $CH_3COCH_2.Sn(CH_3)_3$ with *sym*-TNB in DMSO, as shown by the ^1H NMR spectrum[88].

In the study of the structure of Janovsky σ-complexes obtained from *sym*-TNB derivatives one of the fundamental controversial problems is the site of addition of the acetone residue: to an unsubstituted ring carbon atom in polynitrobenzene or to a carbon atom attached to a substituent. Thus, as a result of the study of the interaction of substituted 1-X-2,4,6-trinitrobenzenes (X = OEt, OPh, Cl, or NMe_2) with acetone in the presence of amines, Foster et al.[70] showed that, in contrast to Kimura's ideas[73], the acetone residue adds to an unsubstituted ring carbon atom with formation of compound (XXI). According to their data, an acetone solution of picryl chloride and triethylamine gives rise to an ^1H NMR spectrum corresponding to structure (XXI, X = Cl) and not (XXII, X = Cl) (triplet with δ = 5.2 p.p.m. and J = 6 Hz).

Kimura et al.[89] isolated by thin-layer chromatography the products formed when acetone solutions of 2,4,6-trinitroanisole and phenyl 2,4,6-trinitrophenyl ether are acted upon by sodium methoxide. The structure of the σ-complex (XXI, X = OCH_3) was demonstrated by ^1H NMR (Table 3) and by the fact that its decomposition in an acid medium yielded 3-acetonyl-2,4,6-trinitroanisole. The same workers[90] investigated analogous σ-complexes of picryl chloride and sodium 2,4,6-trinitrobenzenesulphonate. They believe that the Janovsky reaction results in both cases in the formation of the σ-complexes (XXI, X = Cl or $NaSO_3$) and, when X = $NaSO_3$, also a small amount of (XXII).

The problem of the site of addition of the acetone residue to 1-X-2,4,6-trinitrobenzenes was finally solved in a series of studies[91,92]. It was shown[90] that, when the σ-complex of *sym*-TNB with KOH (XXIII, X = H) is acted upon by acetone, the HO^- ion is displaced by the acetone residue. This is indicated by the change in the electronic spectra [the maxima at 440 and 520 nm are converted into the maxima at 470 and 574 nm corresponding to the σ-complex (XXI)] and by the identification of complex (XXI) by ^1H NMR and infrared spectra. The products of the addition of acetone to 1-X-2,4,6-trinitrobenzenes (X = Me, OMe, COOH, COOMe, COO^-, Cl, or SMe) were isolated in a free state[92] and their structure, like that of the σ-complexes (XXI), was confirmed by elemental analysis, ^1H NMR, and infrared spectra (Table 3). Thus the acetone residue always adds to an unsubstituted carbon atom regardless of the electron-donating or electron-accepting nature of the substituent. According to the authors[92], the steric hindrance to the incorporation in the ring of the fairly bulky CH_2COCH_3 substituent plays the main role here. The $C-CH_2$ bond formed in this process is stronger than the C–O bond in the Meisenheimer complexes (XX), which prevents the isomerisation of the Janovsky σ-complexes (XXI) to complexes (XXII). Both these factors are more significant than the stabilisation of the σ-complex (XX) or (XXII) caused by the energy gain as a result of the weakening of the steric interactions of the substituent X with neighbouring nitro-groups in the course of the formation of the complex. Even in the presence of the electron-accepting substituent COOMe the appearance of an additional positive charge on the $C_{(1)}$ atom does not alter the general features of the addition process. As a result, when *sym*-TNB derivatives interact with acetone, the formation of σ-complexes of type (XXI) becomes preferred both kinetically and thermodynamically.

Table 3. The electronic and ^1H NMR spectra of type (XXIVa) complexes of *sym*-TNB and its derivatives[a].

X	Electronic spectra								^1H NMR spectra							
	λ_1, nm	lg ε_1	λ_2, nm	lg ε_2	λ_3, nm	lg ε_3	Solvent	Refs.	δ H^α (doublet)	δ H^β (triplet)	H^X	δ H^ε	δ H^η	$J_{\alpha,\beta}$	$J_{\beta,\varepsilon}$	Solvent	Refs.
H	572	4.267	464	4.569	—	—	Acetone	95, 92	8.45; 8.35	5.18; 5.08	—	—	—	1.0; 1.0	9.0; 5.5	[D6]acetone	83
																[D6]acetone	70, 111
H	560	—	465	—	—	—	Acetone	56	8.40; 8.31	5.20; 5.04	—	2.87; 2.61	2.03; 2.13	—	6.9; 5.5[b]	[D6]acetone	83
																[D6]acetone	84, 92
H	557	4.104	464	4.434	248	4.007	Methanol	84, 92	8.36	5.08	—	2.00	—	—	—	DMSO	83, 86, 88
H	560	4.076	460	4.408	—	—	Methanol	84	8.41	5.10	—	—	—	—	—	CH_3CN	83
CH_3	539	4.134	461	4.337	—	—	Acetone	56, 34 92, 30	8.47	5.20	2.51	2.46	2.13	—	6.0	[D6]acetone	92
CH_3	536	—	461	—	242		Diglyme	92	—	—	—	—	—	—	—	—	—
OCH_3	534	4.134	444	4.403	—	—	Acetone	92, 89, 90	8.40	5.18	3.94	—	—	1.0	6.0	[D6]acetone	89
OCH_3	520	4.086	445	4.335	246	3.882	Methanol	92	8.37	5.13	3.85	2.51	2.15	—	6.0	[D6]acetone	92
OC_2H_5	510	—	445	—	—	—	Acetone	76	8.35	5.30	—	—	—	2.0	6.0	Acetone	70
OC_6H_5	—	—	—	—	—	—	—	—	8.50	5.20	—	—	—	2.0	6.0	Acetone	70
Cl	518	4.021	446	4.173	—	—	Acetone	92, 73	8.45	5.20	—	—	—	2.0	6.0	Acetone	70
Cl	505	4.100	450	4.230	258	4.072	Methanol	92	8.45	5.22	—	2.58	2.11	—	6.5	[D6]acetone	92
$COOCH_3$	560	3.998	456	4.314	—	—	Acetone	92	8.37	5.12	3.60	2.56	2.15	—	6.0	[D6]acetone	92
$COOCH_3$	550	3.987	456	4.297	250	3.975	Methanol	92	—	—	—	—	—	—	—	—	—
SCH_3	542	3.932	462	4.173	—	—	Acetone	92	8.33	5.34	2.32	2.46	2.14	—	6.5	Acetone	92
$COOC_2H_5$	555	—	450	—	—	—	Acetone	73	—	—	—	—	—	—	—	—	—
$N(CH_3)_2$	—	—	425	—	—	—	Acetone	73	8.37	5.35	—	—	—	1.0	7.0	Acetone	70
3,5-$(CH_3)_2$	590	3.77	480	3.919	—	—	Acetone	92	—	5.16	2.30	2.48	2.05	—	5.5	Acetone	92
3,5-$(CH_3)_2$	566	—	464	—	254	—	Diglyme	92	—	—	—	—	—	—	—	—	—
O^-	420	—	326	—	238	—	Water	100	8.74	4.99	—	2.86	2.25	—	6.0	D_2O	100

a) R = $CH_2^{\varepsilon}COCH_3^{\eta}$; b) $(CH_3)_3\overset{+}{N}H$ cation, δ$(CH_3)_3$ = 2.85 p.p.m.

2,4,6-Trinitrobenzoic acid and its potassium salt undergo extremely rapid decarboxylation and it is possible to obtain[92] only the σ-complex (**XXVIIIa**) of *sym*-TNB and acetone. The study of the ultraviolet spectra of all the σ-complexes in methanol revealed a third maximum in the range 240–260 nm, which probably corresponds to the $\pi-\pi^*$ charge transfer within the cyclohexadiene system (Table 3).

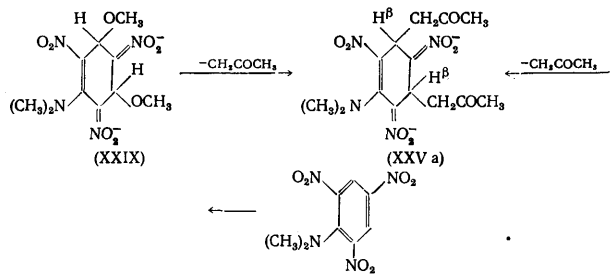
Recent studies[93] of the infrared spectra of the σ-complexes of polynitro-compounds with acetone and alkoxides permitted an unambiguous assignment of the most intense bands in the range 1100–1300 cm^{-1} to the symmetrical stretching vibrations of the negatively charged nitro-group [$\nu_S(NO_2^-)$]. Moderately intense bands near 1500 cm^{-1} apparently correspond to the $\nu_{as}(NO_2^-)$ vibrations. Conclusions concerning the assignment of these bands to the ν_S and ν_{as} frequencies of the NO_2^- group have been confirmed[94] by polarisation Raman spectra.

It has also been shown[95] that the Janovsky σ-complexes as well as the Meisenheimer complexes (**XX**) exhibit a fluorescence at reduced temperatures (77 K) characterised by a single long-wavelength band in the ranges 15 700–16 400 cm^{-1} [compound (**XXVIIIa**)] and 15 630–17 010 cm^{-1} [compound (**VII**)]; the intensity of the luminescence of the *sym*-TNB complex (**XXVIIIa**) is much higher and the spectrum of its polycrystalline form shows a splitting of the band into the two maxima.

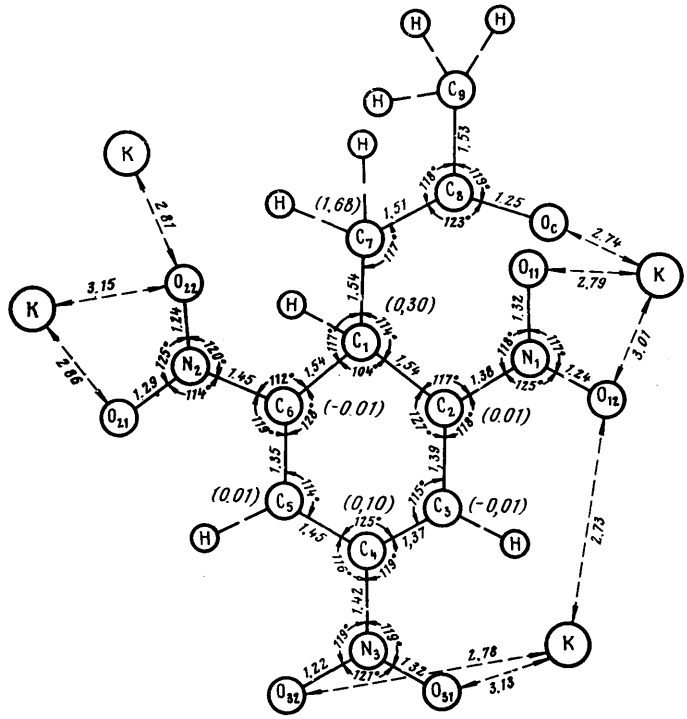
The structure of the Janovsky σ-complex of *sym*-TNB (**XXVIIIa**) has also been demonstrated by X-ray diffraction studies[96], the results of which are presented in the Figure. It was shown that the ring is non-planar–the $C_{(1)}$ and $C_{(4)}$ atoms deviate from the plane of the $C_{(2)}$, $C_{(3)}$, $C_{(5)}$, and $C_{(6)}$ atoms by 0.30 and 0.11 Å respectively and are in the *cis*-position. The $C_{(1)}-C_{(2)}$ and $C_{(1)}-C_{(6)}$ bonds are single (1.54 Å), while the $C_{(2)}-C_{(3)}$ and $C_{(5)}-C_{(6)}$ bonds are predominantly double (see Figure), which demonstrates the overall quinonoid structure of this salt. The acetone residue is located in the plane perpendicular to that of the quinonoid part of the molecule. It is therefore more accurate to represent Janovsky σ-complexes by quinonoid structures of type (**XXVIII**) and (**VII**), despite the fact that in the majority of latest studies structures of type (**XI**) and (**X**) are quoted to take into account the delocalisation of the charge of the anion between the nitro-groups and the ring.

Thus application of the ^1H NMR method combined with electronic and infrared spectroscopic data as well as X-ray diffraction analysis finally established the structure of Janovsky complexes. They are products of the addition of acetone in the keto-form to an unsubstituted carbon atom of an aromatic ring with formation of a C–C bond; structures (**IV**), (**V**), (**X**), and (**XI**) are formed from *m*-DNB and its derivatives, while *sym*-TNB gives rise to structures (**XXIV**) and (**XXVIII**). The data obtained at the present time for the electronic and ^1H NMR spectra of these complexes are presented in Tables 1–3.

(**XXVa**, X = NMe_2), which is also formed when an acetone solution of *N*,*N*-dimethylpicramide is treated with a large excess of triethylamine. The product was identified by ^1H NMR (δH^β = 4.7 p.p.m.).



(2)



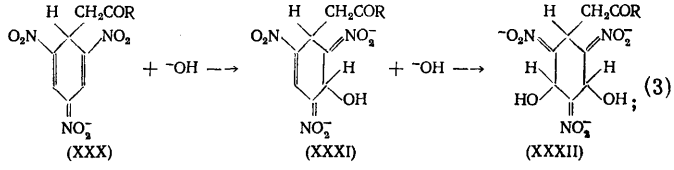
The geometry of the molecule of the σ-complex of *sym*-TNB with acetone (**XXVIIIa**). The distances (in Å) between the atoms of the anion and the $C_2C_3C_5C_6$ plane are given in brackets.

3. Multicharged Janovsky Complexes

In many cases the interaction of polynitro-compounds with acetone in an alkaline medium has been found to entail the formation of doubly and triply charged complexes, either as a result of the addition to the substrate of several acetone residues or as a result of the ionisation of substituents in the aromatic nitro-compound. Thus Foster et al. reported[70] that, when the σ-complex (**XXIX**) is dissolved in acetone, it is solvolysed with formation of the complex

A dianionic complex of *sym*-TNB and acetone of type (**XXV**) was also obtained[97] in the presence of an excess of tetraethylammonium hydroxide. Its structure was demonstrated by electronic (λ_{max} = 516 nm) and infrared spectra [ν(C=O) = 1700 cm^{-1}, $\nu(NO_2^-)$ = 1110 cm^{-1}] as well as the splitting constants for the ESR spectrum of the radical-trianion obtained by its electrochemical reduction. It is suggested that this product has a non-planar structure.

The first doubly charged mono-complexes of type (VI) were isolated a long time ago by Akatsuka[45,46]. In a series of studies[98-100] involving the investigation of the absorption spectra and of the structures of the acid decomposition products, a general mechanism was proposed for the reactions occurring following the addition of NaOH to solutions of the σ-complexes (XXXa) in water[98] and (XXXb) in dimethylformamide (DMF).[99]

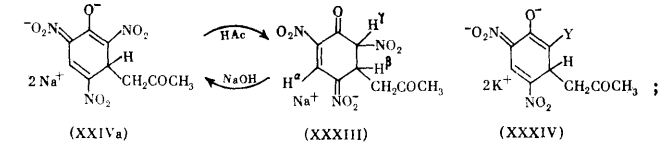


(3)

(XXX) (XXXI) (XXXII)

R=CH_3 (a) or C_6H_5(b).

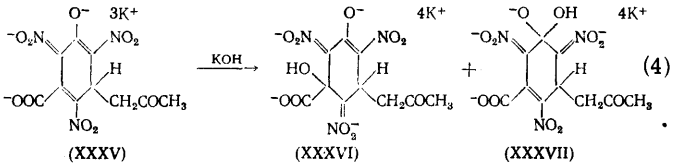
An analogous mechanism has been proposed for the conversion of the σ-complex of *sym*-TNB and cyclohexanone and a dianionic complex of type (XXXI) was isolated in a free form. The σ-complex (XXIVa) was subsequently obtained[100] (and identified) in similar reactions with picric acid. The complex is converted in an acid medium[101] into the complex (XXXIII), from which it can be regenerated by treatment with an excess of alkali.



(XXIVa) (XXXIII) (XXXIV)

Y = $COOCH_3$ (a) or COO^- (b).

On treating an acetone solution of 3,5-dinitrosalicylic acid with an alcoholic solution of KOH, Kovar[102-104] isolated the product (XXXIVb); the absorption spectrum of this complex is analogous to that of the corresponding methyl ester (XXXIVa), which was identified by ^{1}H NMR. The structure of the coloured crystalline σ-complexes (XXIVa) and (XXXVa), obtained similarly from picric and 3-hydroxy-2,4,6-trinitrobenzoic acids, was demonstrated by their chemical reactions and ^{1}H NMR. When one mole of 3-hydroxy-2,4,6-trinitrobenzoic acid is mixed with three moles of KOH in acetone, the σ-complex (XXXV) is formed; it was isolated in a free state and identified on the basis of its ^{1}H NMR and infrared spectra[104,105]. This product is converted into quadruply charged complexes (XXXVI) and (XXXVII) via the mechanism



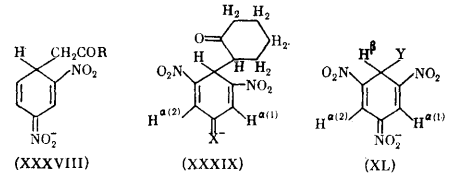
(4)

(XXXV) (XXXVI) (XXXVII)

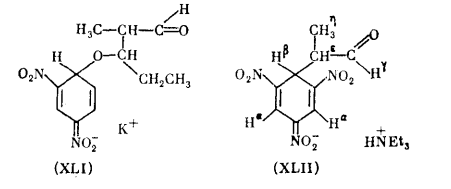
III. PRODUCTS OF THE ADDITION OF OTHER COMPOUNDS WITH MOBILE HYDROGEN ATOMS TO AROMATIC POLYNITRO-DERIVATIVES

By allowing *m*-DNB to interact with acetophenone in an alkaline medium, King and Newall[106] obtained a labile coloured product, whose decomposition with acid yields 2,4-dinitrobenzyl phenyl ketone, which indicates the addition of acetophenone in the keto-form to *m*-DNB. Pollitt and Saunders[44] showed that the characteristics of the formation of σ-complexes of types (IV) and (V) and of the blocking effect of substituents observed for acetone are largely retained in the reactions of *m*-DNB and its derivatives with cyclohexanone, diethyl malonate, cyclopentadiene, and di-n-butyl phosphite in DMF in the presence of NaOH. The relative yield of complexes of type (IV) then increases for cyclopentanone and cyclohexanone, while the reaction with di-n-butyl phosphite yields mainly complex (V). The σ-complexes of *m*-DNB and the ketones CH_3COR (R = Me, Et, n-Pr, n-Bu, iso-Bu, n-C_5H_{11}, and n-C_7H_{15}), obtained by Bronshtein et al.,[107] have been shown by correlation analysis of the oscillator strengths to be the addition products (XXXVIII). When ethyl methyl ketone was allowed to interact with *m*-DNB, 2,4-dinitroanisole, and *sym*-TNB in the presence of KOH, the σ-complexes (XXXVIII, R = Et), (IV, X = OMe, R = $CH_2COC_2H_5$), and (XXX, R = Et), in which the ketone residue is attached to an unsubstituted ring carbon atom, were isolated in a free state[108]. It has been shown by ^{1}H NMR[59] that the reaction of 3,5-dinitrobenzonitrile with diethyl ketone in DMSO in the presence of triethylamine leads to the formation of two isomeric σ-complexes of types (X) and (XI, X = CN) (Table 2).

The products of the interaction of *sym*-TNB with various ketones have now been more fully investigated. The products of the addition of cyclohexanone to *sym*-TNB have been isolated[109] in the form of alkali and alkaline earth metal salts, for which the structure (XXXIX, X = NO_2) has been postulated.



(XXXVIII) (XXXIX) (XL)



(XLI) (XLII)

Foster and Fyfe[84] investigated for the first time by ^{1}H NMR the products, obtained in a free form, of the interaction of *sym*-TNB with ethyl methyl ketone, diethyl ketone, and isopropyl methyl ketone in the presence of triethylamine. Elemental analysis and the electronic spectra correspond in all cases to type (XL) products of the addition of one ketone molecule to *sym*-TNB. The positions of the signals in the ^{1}H NMR spectrum, their relative intensities, and the spin–spin interaction constants in Table 4 established that compound (XLa) is formed in the case of diethyl ketone; only compound (XLb) has been isolated for isopropyl methyl ketone, while the reaction with ethyl methyl ketone results in the formation of both isomers, (XLc) and (XLd), in proportions of 4 : 1. In the study of acetonylacetone the authors were unable to isolate the σ-complex in a free form, while the study of ^{1}H NMR spectra in solution showed that the reaction entails the formation of a mixture of two isomers, (XLe) and (XLf), in proportions of 3 : 1. The splitting of the

signals due to the $H^{\alpha(1)}$ and $H^{\alpha(2)}$ protons, caused by the asymmetry of the $C_{(1)}$ ring atom, has been observed[110] in the ^{1}H NMR spectra of a number of σ-complexes of *sym*-TNB with bulky substituents Y[compound(XL, g–j)](Table 4). The authors believe that the temperature variation of the splitting confirms the view that it is due to the hindered rotation about the C–C bond between the rings in σ-complexes of type (XL). An analogous phenomenon has recently been observed[111] for the σ-complexes (XXXIX) of 1-X-3,5-dinitrobenzenes with cyclohexanone (Table 2).

Table 4. Electronic and ^{1}H NMR spectra of the σ-complexes of 1,3,5-trinitrobenzene with various nucleophiles containing a mobile hydrogen atom.

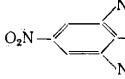
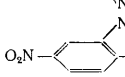
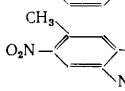
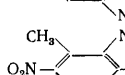
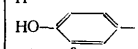
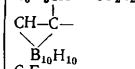
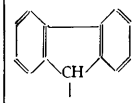
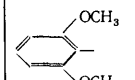
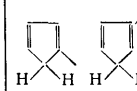
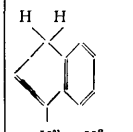
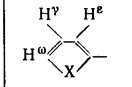
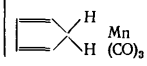
Structure	Y	Cation	Electronic spectra					^{1}H NMR spectra				Solvent[a]	Refs.
			λ_1, nm	lg ε_1	λ_2, nm	lg ε_2	Solvent[a]	δ H^α	δ H^β	$J_{\beta,e}$	$J_{\alpha,\beta}$		
(XLa)	$CH_3CH_2COCH^eCH_3$	$HNEt_3^+$	550	4.09	465	4.40	M	8.45	5.31	3.0	1.0	DMSO	84, 110
(XLb)	$(CH_3)_2CH-COCH^e_2-$	$HNEt_3^+$	550	4.07	466	4.41	M	8.34	5.05	6.0	—	DMSO	84
(XLc)	$CH_3CH^eCOCH_3$	$HNEt_3^+$	—	—	—	—	—	8.46	5.35	3.0	—	DMSO	84
(XLd)	$CH_3CH_2COCH^e_2-$	$HNEt_3^+$	—	—	—	—	—	8.35	5.04	6.0	—	DMSO	84
(XLe)	$CH_3COCH_2CH_2COCH^e_2-$	$HNEt_3^+$	—	—	—	—	—	8.35	5.07	5.0	—	DMSO	84
(XLf)	$CH_3CO-CH^e-CH_2COCH_3$	$HNEt_3^+$	—	—	—	—	—	8.45	5.35	3.0	—	DMSO	84
(XLg)	$C_6H_5CH^eCOCH_2C_6H_5$	$HNEt_3^+$	—	—	—	—	—	8.4 (1); 8.3 (2)	5.74	3.0	1.0	DMSO	110, 217
(XLh)	$C_6H_5CH^e-CN$	$HNEt_3^+$	—	—	—	—	—	8.32 (1); 8.21 (2)	5.47	3.5	1.0	DMSO	110
(XLi)		$HNEt_3^+$	—	—	—	—	—	8.37 (1); 8.30 (2)	5.01	0.7	1.0	DMSO	110
(XLj)		$HNEt_3^+$	—	—	—	—	—	8.33 (1); 8.21 (2)	5.33	—	2.5	DMSO	110
(XL)	$P(OEt)^b_3$	—	570	—	471	—	DMSO	8.53	5.45	—	2.5	DMSO	129
(XL)	$P(OMe)_3$	—	578	—	470	—	DMSO	8.50	5.44	—	2.5	DMSO	129
(XL)	$P(OEt_2)Ph$	—	591	—	481	—	DMSO	8.43	5.18	—	2.0	DMSO	129
(XL)	$P(NMe_2)_3$	—	599	—	486	—	DMSO	8.54	5.66	—	2.0	DMSO	129
(XL)	NO_2CH_2-	K^+	568	4.04	456	4.34	DMSO	8.41	5.35	—	7.5	DMSO	131
(XL)	CH_3CHNO_2	$HNEt_3^+$	552	4.08	452	4.38	DMSO	8.47	5.67	0.5	3.2	DMSO	131
(XL)	$(CH_3)_2C-NO_2$	$HNEt_3^+$	545	4.06	450	4.36	DMSO	8.51	5.90	1.4	0.0	DMSO	131
(XL)	$CH_3CH_2CHNO_2$	$HNEt_3^+$	552	4.04	452	4.34	DMSO	8.46	5.63	1.0	3.5	DMSO	131
(XXI)	$R=NO_2CH_2-$[c]	$HNEt_3^+$	490	—	—	—	Al	8.40	5.77	5.0	1.0	DMSO	131
(XLIVa)	CH_3SO-CH_2-	K^+	518	—	440, 490[f]	—	DMSO	8.34	6.83	—	—	[D_6]DMSO	136
(XL)	$(CH_3)_2NCO-$	K^+	510	—	440	—	DMSO	8.20	6.71	—	—	[D_6]DMSO	135
(XL)	$(CH_3)_2NCOCH_2-$	K^+	520	—	442	—	DMSO	—	—	—	—		136
(XL)	$CH_3C(CN)NEt_3$	—	560	—	447	—	DMSO	8.5; 8.4	5.00	—	2.0	[D_6]DMSO	138
(XL)	$-CH^{ee}_3$	$As^+(Ph)_4$	572	4.17	470	4.50	Al	8.24	4.64	6.2	0.75	[D_3]Al	149
(XL)	$-C_4H_9$	$N^+(CH_3)_4$	563	4.17	474	4.50	Al	8.39	4.84	4.2	0.75	[D_3]Al	149
(XL)		K^+	570	—	461	—	DMSO	8.31	5.17	6.0	—	[D_6]DMSO	153, 154
(XL)		K^+	570	—	462	—	DMSO	8.08	5.10	—	—	[D_6]DMSO	153
(XL)		K^+	568	—	468	—	DMSO	8.15	5.19	5.5	1.0	[D_6]DMSO	153, 154
(XL)		K^+	570	—	468	—	DMSO + M	8.15	5.09	5.5	—	[D_6]DMSO	153
(XL)	CCl_3	Na^+	495	—	427	—	E	8.61	6.35	—	—	[D_6]DMSO	155, 156
(XL)	CBr_3	Na^+	490	—	430	—	E	8.53	6.34	—	1.5	[D_6]DMSO	156
(XL)	Cl_3	Na^+	—	—	—	—	—	8.48	5.69	—	1.5	[D_6]DMSO	156
(XXII)	$R=CH_3COCHCOOC_2H_5$[f]	K^+	—	—	—	—	—	8.60	—	—	—	[D_6]DMSO	119
(XLIV)	$NO_2CH^g_2$	$HNEt_3^+$	562	—	—	—	Al + DMSO	8.30	4.18	—	—	Al + DMSO	131

Table 4 (Cont'd).

Structure	Y	Cation	Electronic spectra					^{1}H NMR spectra				Solvent[a]	Refs.
			λ_1, nm	lg ε_1	λ_2, nm	lg ε_2	Solvent[a]	δH^{α}	δH^{β}	$J_{\beta,\varepsilon}$	$J_{\alpha,\beta}$		
(XL)	H	$\overset{+}{N}(CH_3)_4$	585	4.18	478	4.49	Al	8.26	3.88	—	0.5	Al	143
(XLVII)	H[3]	$\overset{+}{N}(CH_3)_4$	550	4.53	478	4.44	Al	8.24	3.87	—	—	[D$_6$]DMSO	145
(L a)	H	$\overset{+}{N}(CH_3)_4$	—	—	—	—	—	8.35	4.04	—	—	[D$_6$]DMSO	145
(L b)	H[i]	$\overset{+}{N}(CH_3)_4$	—	—	—	—	—	8.35	3.92	—	—	[D$_6$]DMSO	145
(L c)	H[j]	$\overset{+}{N}(CH_3)_4$	580	4.53	478	4.40	Al	8.38	3.90	—	—	[D$_6$]DMSO	145
(XL d)	HO–	K^+	570	—	468	—	DMSO + M	8.44	5.62	—	—	[D$_6$]DMSO	157
(XL)	$C_6H_5CH^e(CO_2C_2H_5)_2$	Na^+	—	—	—	—	—	8.30	5.67	4.6	2.1	[D$_6$]DMSO	87
(XL)		Na^+	—	—	—	—	—	8.48	5.90	—	—	[D$_6$]DMSO	87
(XL)	C_6F_5	Na^+	—	—	—	—	—	8.48	6.10	—	—	[D$_6$]DMSO	87, 88
(XL)	$(CF_3)_2CH$–	Na^+	—	—	—	—	—	8.46	5.58	—	—	[D$_6$]DMSO	87
(XL)	CN	Na^+	—	—	—	—	—	8.40	5.70	—	—	[D$_6$]DMSO	87
(XL)		$\overset{+}{Sn}(CH_3)_3$	—	—	—	—	—	8.50	5.80	—	—	DMSO	88
(XL m)		PyH$^+$	585	4.75	475	4.43	P	8.35	6.32	—	0.2	[D$_6$]DMSO	160
			—	—	—	—	—	8.21	6.53	—	1.3	[D$_6$]Al	160
			—	—	—	—	—	8.12	6.44	—	1.3	[D$_6$]D	160
(XL)		PyH$^+$	520	—	437	—	P	8.82 & 8.79	5.59 & 5.88	—	—	[D$_5$]P	163
								8.40	5.62	—	—	[D$_6$]DMSO	163
								8.55	5.75	—	—	[D$_6$]An	163
(XL i)		PyH$^+$	580	4.18	475	4.48	P	8.90	6.14	—	—	[D$_5$]P	163
								8.86	6.08	—	—	[D$_6$]An	163
(XL)	 X=O[k]	PyH$^+$	—	—	—	—	—	8.73	5.86	—	<0.3	[D$_6$]DMSO	164
(XL)	X=S[l]	PyH$^+$	558	4.18	454	4.48	An	8.73	6.00	—	<0.3	[D$_6$]DMSO	164
(XL o)		PyH$^+$	550	—	460	—	P	8.45	5.65	—	—	DMSO	165

a) M = methanol, DMSO = dimethyl sulphoxide, Al = acetonitrile, E = ethanol, An = acetone, P = pyridine, D = dioxan; b) $J_{\alpha,\beta}$ = 21 Hz, $\delta(CH_2)$ = 4.5 p.p.m., $\delta(CH_3)$ = 1.53 p.p.m.; c) X = $N(CH_3)_2$; d) inflection; e) $\delta(CH_3)$ = 1.14 p.p.m.; f) X = OCH_3, δH = 3.4 p.p.m.; δ = 3.8(2H), 2.2(3H), and 1.1(3H) for R; g) R = H^{γ}, δH^{γ} = 5.38 p.p.m., δH^{ω} = 6.59 p.p.m.; $J_{\omega,\gamma}$ = 10.2 Hz, $J_{\alpha,\gamma}$ = 1.9 Hz, $J_{\beta,\omega}$ = 5.0 Hz; h) λ_3 = 262 nm, lg ϵ_3 = 4.18, $\delta[\overset{+}{N}(CH_3)_4]$ = 3.12 p.p.m.; i) $\delta(OCH_3)$ = 3.76 p.p.m.; j) λ_3 = 256 nm, lg ϵ = 4.04, $\delta(CH_3)$ = 2.58 p.p.m.; k) $J_{\epsilon,\gamma}$ = 6.6 Hz, $J_{\epsilon,\omega}$ = 0.8 Hz, $J_{\gamma,\omega}$ = 1.18 Hz; l) $J_{\epsilon,\gamma}$ = 6.4 Hz, $J_{\epsilon,\omega}$ = 1.1 Hz, $J_{\gamma,\omega}$ = 5.3 Hz.

Thus the Janovsky reaction with various ketones exhibits the characteristics described above for acetone. Furthermore, in many instances isomers are formed due to the presence of several reaction centres in complex ketones. The non-equivalence of the $H^{\alpha(1)}$ and $H^{\alpha(2)}$ protons has been observed for ketones with bulky substituents.

Very much less attention has been devoted to the interaction of polynitro-compounds with aldehydes. A spectrophotometric study of this reaction for a series of aldehydes showed[112] that the first stage is aldol condensation of the aldehydes, after which the polynitro-compound combines with the aldol alkoxide to form a σ-complex of type (XLI). Having isolated the product of the interaction of propionaldehyde with *m*-DNB, Gitis and Kaminskii[113] concluded somewhat later that this involves the addition of the aldol—the product of the condensation of four molecules of the initial aldehyde—to *m*-DNB. After treating *sym*-TNB with triethylamine in propionaldehyde, Strauss[114] isolated a crystalline product, to which he proposed structure (XLII) on the basis of elemental analysis and infrared [ν(C=O) = 1720 cm^{-1}] and visible (λmax = 470 and 566 nm in methanol) spectra. This structure was also confirmed by the ^{1}H NMR spectrum. Thus in this case the aldehyde reacts like ketones, which may be due, on the one hand, to

the greater reactivity of *sym*-TNB compared with *m*-DNB and, on the other, to the smaller capacity of diethylamine (compared with KOH) to induce aldol condensation.

The interaction of *m*-DNB with ethyl malonate, phenylacetate, and cyanoacetate in the presence of aqueous KOH yielded coloured solutions whose absorption maxima are in the same part of the spectrum as for the products of the reaction with acetone (515 ± 15 nm). On this basis, the authors[23-25,31] believe that the structures of the complexes are the same in all cases.

However, there are few reliable data on the structures of such products. In an early study Jackson and Gazzolo[115] isolated the products of the addition of the sodium derivatives of malonic and acetoacetic esters to *sym*-TNB and 2,4,6-trinitroanisole in proportions of 3 : 1. Their insignificant stability indicates, according to the authors, an addition reaction with formation of a C–O bond and not a C–C bond. The products of the addition of two molecules of sodium derivatives of acetophenone, benzyl cyanide, and malonic and cyanoacetic esters to *m*-DNB have been obtained[14]. Shein and Ivanova[116] showed that the σ-complex isolated by Baudet[117] in the reaction of equivalent amounts of 1-fluoro-2,4-dinitrobenzene with malonic ester in the presence of triethylamine is a mixture of the initial 1-fluoro-2,4-dinitrobenzene, diethyl 2,4-dinitrophenylmalonate, and ethyl α,α-bis(2,4-dinitrophenyl)acetate. By treating[118] 9-nitroanthracene with the sodium derivatives of malonic ester, methylmalonic ester, nitropropane, etc. in DMSO, intensely coloured solutions, evidently containing the σ-complexes [XVIIb, Y = $CH(CO_2Et)_2$, $C(CH_3)(CO_2Et)_2$, $C(CH_3)_2NO_2$, $CH(CN)_2$, etc.], were obtained; after acidification, they are converted quantitatively into the corresponding derivatives of dihydroanthracene.

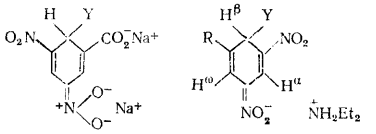
The only study where the structure of coloured products of this type was demonstrated unambiguously is that of Strauss[119], who treated a tetrahydrofuran solution of 2,4,6-trinitroanisole with an excess of acetoacetic ester in the presence of potassium butoxide and isolated the 1 : 1 adduct [XXII, X = OMe, R = $CH(COCH_3)COOEt$]. Its structure was established by elemental analysis and ^1H NMR (Table 4); on treatment with an acid, the OMe group is split off and ethyl α-picrylacetoacetate is formed.

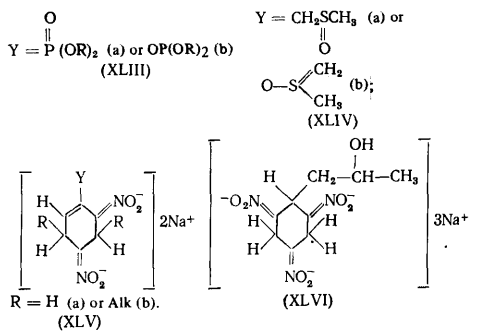
After surveying the entire data accumulated at the time, Foster and Mackie[37] concluded, following Canbäck[23-25], that not only carbonyl compounds but also many other substances with a fairly mobile hydrogen atom can react successfully with polynitro-compounds. Indeed, instances of the employment of uric acid and a number of amino-acids[18], laevulose, glucose, and other sugars[22,23], instead of acetone, in the colour reaction have been described. On the other hand, if the ion of the conjugate base is extremely stable, no colour is produced[37]. Many dialkyl and alkyl aryl ketones and derivatives of fluorene, indene, phenanthrene, etc. give rise to an intense violet colour on reaction with *o*-dinitrobenzene or 2,2′-dinitrobiphenyl in DMF in the presence of tetrabutylammonium hydroxide[120-123]. In many instances a colour appears on interaction of *m*-DNB and its derivatives with DMF in the presence of alkali[121,124].

Numerous studies have been made on the interaction of *sym*-TNB and *m*-DNB with compounds having a mobile hydrogen atom. Saunders and Stark[125] suggested that coloured products (XLIIIa) or (XLIIIb) are formed in the reaction of 3,5-dinitrobenzoic with dialkyl phosphites. Alkylphosphine oxides in the presence of 30% NaOH[126], methylenediphosphonates[125], di-isopropyl ethynylphosphonate[127], alkyltriphenylphosphonium salts[120], and quaternary α- and γ-picolinium salts[128] give rise to a similar colour reaction. It has been shown recently[129] that trialkyl phosphites, phosphorimidites, phosphonites, phosphinites, and dialkyl phosphorofluoridites (but not triphenyl phosphite) react readily with *sym*-TNB in DMSO to form σ-complexes of type (XL), which are converted in solution into the corresponding phosphoryl compounds ($ArPOR'R''$). Some of the σ-complexes [XL, Y = $\overset{+}{P}(OMe)_3$, $\overset{+}{P}(OEt)_3$, $\overset{+}{P}(OEt)_2Ph$, or $\overset{+}{P}(NMe_2)_3$] have been identified with the aid of ^1H NMR and electronic spectra (Table 4). It is believed[129] that phosphorylation of *sym*-TNB and its halogeno-derivatives by phosphorus(III) compounds proceeds via the intermediate formation of σ-complexes of type (XXII, X = H, F, or Cl, R = $\overset{+}{P}R_3$), whose stability is to a large extent determined by the ease of elimination of the substituted group and by the nature of the solvent.

Urbanskii[130] was the first to measure the absorption spectra of the products of the reaction of nitromethane and other nitroalkanes with *m*-DNB and *sym*-TNB in methanol in the presence of NaOH. Subsequently treatment with triethylamine led to the isolation[131] in a free form of σ-complexes of type (XL) after the reaction of *sym*-TNB and *N*,*N*-dimethyl-2,4,6-trinitroaniline with a series of nitroalkanes (Table 4). Their electronic and ^1H NMR spectra are close to the characteristics of the corresponding acetone complexes (Table 3) as well as the σ-complex of *m*-DNB and nitromethane (XLIV, R = H, Y = CH_2NO_2), which has been investigated in solution (Table 4). Furthermore, the formation in reaction solutions of σ-complexes of nitromethane with 1,3-dinitronaphthalene (XVIb) and with 3,5-dinitropyridine has been detected with the aid of electronic and ^1H NMR spectra[131]; in the latter case a mixture of isomers analogous to (XIIIb) and (XIV) is formed.

A study of the reaction of *m*-DNB and a series of 1-R-3,5-dinitrobenzenes (R = H, $CONH_2$, CO_2Et, CO_2Na, etc.) with DMSO led to the conclusion[132,133] that the coloured products have a structure analogous to that of the products of the reaction with acetone and that DMSO may add in the "keto-form" (XLIVa) or in the "enolic" form (XLIVb). In the interaction of $-CH_2SOCH_3$ with *sym*-TNB in DMSO Foster and coworkers[134,135] detected by ^1H NMR the σ-complex (XLIVa) (Table 4), which, however, is rapidly converted into (XXIII, X = H). Soon the σ-complex (XLIVa) was isolated in a free form[136] and its structure was demonstrated; the stretching vibration of the S=O bond is observed in the infrared spectra at 1035 cm^{-1} and that of the $S-CH_3$ groups occurs at 1320 and 1410 cm^{-1}. The same workers[146] isolated type (XL) products of the interaction of *sym*-TNB with DMF or dimethylacetamide, a detailed study of which showed (Table 4) that the addition of a nucleophile takes place also with formation of a C–C bond. It was noted that in acetone and acetonitrile the added DMSO, DMF, etc. anions are displaced by the more active anions $-CH_2CN$ and $-CH_2COCH_3$. Certain products of the addition of CH_3CN to polynitro-compounds, namely σ-complexes of type (XXI, X = H or COOH, R = CH_2CN) as well as (IV) and (V) with X = H or OMe and R = CH_2CN (Table 2) were investigated recently[137] with the aid of electronic, ^1H NMR, and infrared spectra. As in the reactions with acetone and nitromethane, the addition of acetonitrile leads to the formation of a C–C linkage.

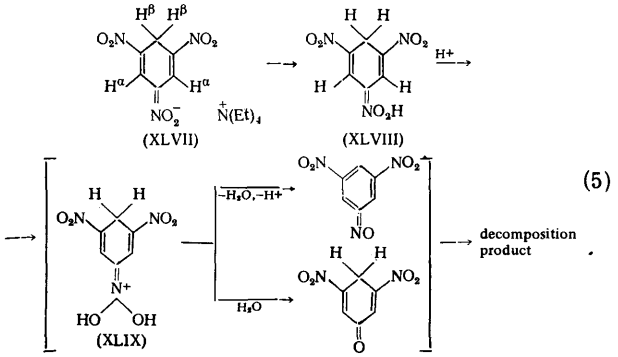




When a solution of *sym*-TNB in acrylonitrile was treated with triethylamine, an extremely unstable 1 : 1 : 1 addition product was isolated[138] after subsequent precipitation with ether. Having analysed its ^{1}H NMR spectra, the authors gave preference to the second of the two possible structures of the zwitter-ions [XL, Y = $-CH(CN)CH_2\overset{+}{N}Et_3$] and [XL, Y = $-C(CH_3)(CN)\overset{+}{N}Et_3$] (Table 4).

In a study of the reduction of *m*-DNB, *sym*-TNB, and its derivatives with sodium tetrahydroborate to the corresponding polynitrocyclohexanes Severin and coworkers[139, 140] suggested the formation of intermediates involving the addition of one (IV or V, R = H, X = H, Cl, Br, Me, COOH, or CH = CHC_6H_5) and then two (XLVa) and three (XXVI, R = H) hydride ions to the initial nitro-compounds. Certain products of type (XLV) were obtained in the form of crystalline salts[141], which proved to be stable in the case of 2,4- and 3,5-dinitroanisoles and labile in the case of *m*-DNB. The structure of the complexes (XLV, Y = OMe, R = H) was demonstrated by their conversion into azabicyclononene derivatives as a result of aminoalkylation. The possibility of the formation of the trianionic complex (XLVI) after the reduction of the σ-complex (XXVIIIa) derived from *sym*-TNB with sodium tetrahydroborate was demonstrated[142]. Although the product (XLVI) was not isolated in a free form, its structure was confirmed by the finding that, on being oxidised with bromine, it is converted into 2-methyl-4,6-dinitrocoumaran.

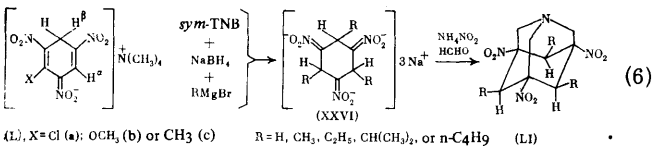
When *sym*-TNB was mixed with tetraethylammonium tetrahydroborate in acetonitrile in an atmosphere of nitrogen, purple crystals of the σ-complex (XLVII) were isolated[143]. Treatment of this complex with sulphuric acid made it possible to obtain[144] the nitronic acid (XLVIII), which is stable only in dilute solutions. Its absorption maximum in chloroform is at 370 nm, while in ethanol two maxima, characteristic of the usual σ-complexes of type (XXVIII), are observed.



(5)

The decomposition of (XLVIII) in an acid medium begins, according to the authors, with the protonation of the nitronic acid (XLVIII) to give the unstable ion (XLIX), which is rapidly dehydrated to form a nitroso-compound or is hydrolysed to cyclohexadienone. To confirm this mechanism, the authors isolated and demonstrated the structures of the decomposition products [3,5-dinitroaniline, *N*-(3,5-dinitrophenyl)hydroxylamine, 3,3′,5,5′-tetranitroazoxybenzene, 3,3′,5,5′-tetranitrohydrazobenzene, bis-(3,5-dinitrophenyl)amine, and 3,5-dinitrophenol]. The hydride complex (XLVII) was also isolated[145] after treating an acetonitrile solution of *sym*-TNB with tetramethylammonium octahydroborate in an inert atmosphere. The hydride complexes of 1-X-2,4,6-trinitrobenzenes (L) were obtained similarly[145]; when X = Cl or OMe, the complexes are isolated in a mixture with (XLVII), the complex (L) being obtained in a pure form only for X = Me†.

The interaction of *sym*-TNB and *m*-DNB with Grignard compounds in the presence of sodium tetrahydroborate, which results in the formation of 1,3,5-trialkyl-2,4,6-trinitrocyclohexanes and dialkyldinitrocyclohexanes respectively, proceeds, according to Severin and coworkers[146,147], via intermediate complexes of type (XLV) and (XXVI) with R = Me, Et, etc. The authors were unable to isolate these products and to investigate their structures, while aminomethylation of (XLVI, R = Me) and (XXVI, R = Me) by formaldehyde and ammonium nitrate makes it possible to obtain[148] a series of trinitroaza-adamantanes (LI), whose structure has been convincingly demonstrated by a number of methods.



(6)

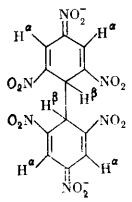
The products of the addition of aliphatic and aromatic hydrocarbons, with fairly mobile hydrogen atoms, to *sym*-TNB were obtained by a number of workers, who either used specific reagents or selected appropriate reaction conditions. Thus, on treating *sym*-TNB in acetone and in an inert atmosphere with tetramethylammonium (or tetraphenylarsonium) tetra-alkylborates, Taylor[149] obtained the σ-complexes (XL, Y = Me or Bu) (Table 4).

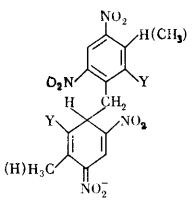
Electrochemical reduction of *sym*-TNB in acetone at a controlled potential, corresponding to the transfer of two electrons, led to the isolation[150] of the "paired" σ-complex (LII)—the product of the interaction of two *sym*-TNB molecules with one another—which has two absorption maxima (at 432 and 510 nm), characteristic of σ-complexes of type (XXVIII). Its ^{1}H NMR spectrum has only two singlets—due to the four H^α protons (δ = 8.01 p.p.m.) and two H^β protons (δ = 5.37 p.p.m.); its infrared spectrum is analogous to that of (XXVIIIa), but there is no ν(C=O) band.

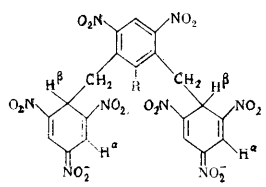
Foster and Mackie[37] observed that solutions of 2,4-dinitrotoluene in alkaline ethanol absorb at ~ 520 nm, which they attributed to the complex (LIII, Y = H). Here 2,4-dinitrotoluene behaves both as an electron acceptor and as a substance with mobile hydrogen atoms. On the other

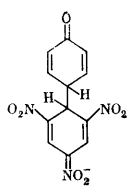
†It has been shown recently[218] that hydride σ-complexes of type (XLVII) can be readily isolated after the interaction of *sym*-TNB with dihydro-derivatives of nitrogen-containing heterocycles: 1,3-dimethylbenzimidazoline, 1,3-dimethylnaphtho[2,3-*d*]imidazoline, 1,3-dimethyl-2,3-dihydropyrimidine, and 1-benzyl-1,4-dihydronicotinamide. A σ-complex of *sym*-TNB with the model coenzyme NADH was also detected, which may be important in biochemistry for the investigation of the mechanism of oxidation-reduction reactions.

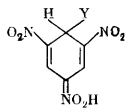
hand, Pollitt and Saunders[44] believe that the long-wavelength maximum (at 648 nm), arising when a solution of 2,4-dinitrotoluene in DMF is treated with NaOH, corresponds to the 2,4-dinitrobenzyl anion and not the complex (LIII, Y = H). This is confirmed by the results of quantum-chemical calculations[151] of its structure and electronic spectra. A study of the kinetics of the rapid reaction of 2,4,6-trinitrotoluene with alkoxides in an alcoholic medium demonstrated the possibility of the formation of the products (LIII, Y = NO_2) with calculated absorption maxima at ~ 450 and ~ 550 nm. However, a compound of this type could not be isolated in a free form and it was investigated in detail much later[153,154]. When 2,4,6-trinitrotoluene is added to a solution of *sym*-TNB in DMSO in the presence of KOH, new maxima, corresponding to the σ-complex [XL, Y = 2,4,6-$(NO_2)_3C_6H_2CH_2$], appear at 465 and 580 nm, instead of the absorption spectrum of the σ-complex with the OH^- ion (XXIII, X = H) formed initially (λ_{max} = 440 and 518 nm).

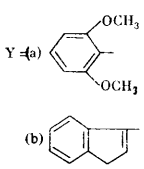

(LII)


(LIII), Y = H, NO_2


R = NO_2 (a); H (b)
(LIV)


(LV)




(LVI)

σ-Complexes of *sym*-TNB with 2,4-dinitrotoluene, 4,6-dinitro-*m*-xylene, and 2,4,6-trinitro-*m*-xylene were obtained similarly (Table 4). In the last two cases treatment with alkali in a polar medium may result in the ionisation of the second methyl group, which entails the formation of the σ-complexes (LIV, a and b) in the interaction with *sym*-TNB. These compounds were also isolated in a free form and identified with the aid of electronic and ^1H NMR spectra. Electronic absorption spectra make it possible to detect similar reactions with *sym*-TNB and other alkyl derivatives of *m*-DNB or *p*-nitrotoluene[154]. Thus it has been established that, under the influence of alkali in aprotic solvents, *sym*-TNB and *m*-DNB derivatives containing methyl groups may behave not only as electron acceptors but also as nucleophiles as a result of the dissociation of a hydrogen atom in the methyl group.

Shein and coworkers[155,156] showed by ^1H NMR that, when the σ-complex of *sym*-TNB with potassium methoxide (XX, Y = NO_2, X = OMe) is treated with haloforms in DMSO in the presence of NaOMe, the stable σ-complexes (XL, Y = CCl_3, CBr_3, or CI_3) are formed, and isolated the first two in a free form (Table 4). Similar reactions occur when weaker bases are used: piperidine, diethylamine, and triethylamine. An interesting case of the formation of a σ-complex with a C–C and not a C–O bond has been described[157]. In accordance with the ambident nature of the phenoxide ion, its slow interaction with *sym*-TNB in a 4 : 1 DMSO–MeOH mixture leads to the σ-complex (LV), which then rearranges to (XLk, Y = *p*-HOC_6H_4). The latter was isolated in a free form (Table 4) and proved to be fairly stable even in weakly acid media.

The use of organometallic compounds as a source of carbanions is of considerable interest. A very novel method has been proposed by Beletskaya and coworkers[86,87], who treated *sym*-TNB with a series of organomercury compounds of the type R_2Hg and RHgX in DMSO in the presence of NaI and obtained a series of new σ-complexes [XL, Y = CHPhCOOEt, $B_{10}H_{10}C_2H$, C_6F_5, $(CF_3)_2CH$, CN, or CCl_3, X = Br], which were identified by ^1H NMR in the reaction solutions (Table 4). σ-Complexes of type (XL) were obtained similarly[88] by employing organotin compounds $RSnMe_3$ (where R = C_6F_5, fluorenyl, cyclopentadienyl, or indenyl, but not alkyl or phenyl) (Table 4). In certain cases a mixture of isomers is formed, for which a complete analysis of ^1H NMR spectra is difficult. The same workers recently synthesised[158] σ-complexes of a new type in which the tetrahedral carbon atom is linked to Si, Ge, and Sn. The compounds R_2EM (R_2E = Me_3Sn, Ar_3Sn, Et_3Ge, or Me_3Si, M = K or Li) were added to a solution of *sym*-TNB in tetrahydrofuran at temperatures down to −30°C in an inert atmosphere. All the σ-complexes obtained have characteristic electronic spectra (λ_1 = 435–440 nm, and λ_2 = 494–500 nm) and ^1H NMR spectra (δH^{α} = 8.30–8.40 p.p.m., δH^{β} = 6.10–6.30 p.p.m., 2 : 1 ratio), which confirms their structure. On treatment with acetone, they are converted into the corresponding Janovsky σ-complex (XXVIII).

Wennerström and coworkers[159] showed that, when phenylcopper reacts with *sym*-TNB in pyridine or quinoline at room temperature, an intensely coloured compound is formed. They identified it as a σ-complex on the basis of the characteristic absorption in the visible spectrum (λ_{max} = 444 and 522 nm). For the more stable 2,6-dimethoxyphenylcopper, it was possible to obtain a fairly stable crystalline complex (XLl), which was isolated as the pyridinium salt after acidifying the reaction mass with acetic acid (Table 4). Similar reactions occur, albeit more slowly, with 2,4,6-trimethoxy- and 2,6-dimethoxyphenyl silver[160]. In the latter case acidification of the σ-complex (XLl) with dilute H_2SO_4 made it possible to isolate in a free form 4-(2,6-dimethoxyphenyl)-3,5-dinitrocyclohexa-2,5-dienenitronic acid (LVIa). Its structure was demonstrated with the aid of infrared and ^1H NMR spectra; the ^1H NMR spectrum in DMSO virtually coincides with the spectrum of the corresponding σ-complex (XLl). In a polar medium (pyridine, ethanol) the nitronic acid fully dissociates with formation of the anion (λ_{max} = 470 and 590 nm), in a non-polar medium ($CHCl_3$) the undissociated form predominates (λ_{max} = 360 nm), while in acetone the two forms are in equilibrium and the spectrum shows all three maxima. Analogous results were obtained[161] in a study of the interaction of *sym*-TNB in pyridine with phenylethynylcopper and phenylethenylsilver and with hexylcopper. The formation of coloured σ-complexes (XL, Y = C≡C–Ar) was detected with the aid of electronic spectra (λ_{max} = 442 and 530 nm) and confirmed by the structure of the acid decomposition products isolated, among which the main component is 2,4,6-trinitrotolane.

The interaction of *sym*-TNB with cyclopentadiene[162,163] in pyridine in the presence of silver oxide leads to two isomeric σ-complexes (XL, Y = 1,3- or 1,4-cyclopentadienyl) in approximately equal amounts (Table 4). When *sym*-TNB is acted upon by indene under analogous conditions, the σ-complex with pyridine (XL, Y = ) is

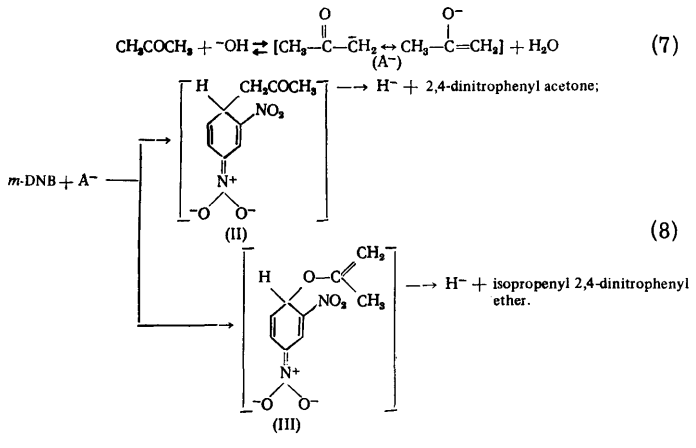
formed initially (λ_{max} = 437 and 520 nm) and is then gradually converted into the σ-complex (XLm), which has been isolated in 87% yield and identified (Table 4). On treatment with H_2SO_4, this complex is converted into 4-(3-indenyl)-3,5-dinitrocyclohexa-2,5-dienenitronic acid (LVIb), which is reconverted under the influence of NaOH into the "indenyl" σ-complex (XLm). The σ-complexes of *sym*-TNB with 2-furyl-, and 2-thienyl-copper (Table 4) have been isolated in a free form at a reduced temperature[164]. The reaction of *sym*-TNB with cyclopentadienylmanganese silver tricarbonyl in pyridine similarly leads to the formation[165] of the corresponding σ-complex (XLn) (Table 4).

Thus the interaction of polynitro-derivatives of aromatic hydrocarbons with various compounds containing mobile hydrogen atoms yields Janovsky σ-complexes in an alkaline medium, in which a C–C bond is formed between a tetrahedral ring carbon atom and a carbon atom of the nucleophile. Under these conditions, their further reduction or acid decomposition in many instances lead to new pathways towards the formation of previously unobtainable aromatic and alicyclic compounds.

IV. KINETICS AND MECHANISM OF THE JANOVSKY REACTION

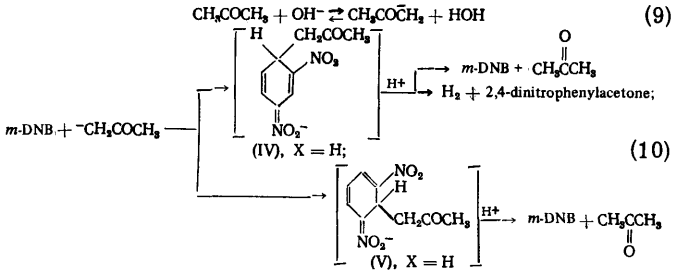
1. The Formation of σ-Complexes

In his review Canbäck[166] examined the mechanisms proposed[14,15,36] for the Janovsky reaction and showed that none is sufficiently convincing. He suggested for the first time[23] that the interaction of *m*-DNB with acetone in an alkaline medium be regarded as nucleophilic substitution of a hydrogen atom in the aromatic ring by the acetone residue in one of its tautomeric forms [Eqn. (7)] with formation of 2,4-dinitrophenylacetone or isopropenyl 2,4-dinitrophenyl ether [(Eqn. (8)]:

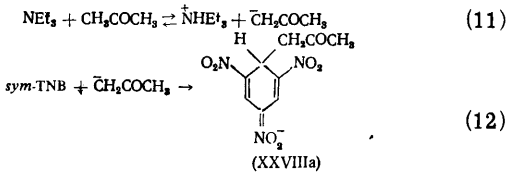


However, all attempts to isolate the final reaction product proved to be unsuccessful.

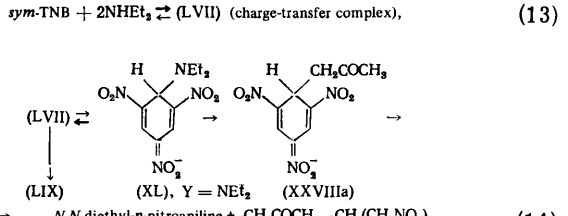
In a number of studies[23,26,120,166] dealing with the mechanism of the Janovsky reaction an analogy is drawn with the mechanism of the formation of type (XX) Meisenheimer σ-complexes[1,6]. In their survey of these ideas, Gitis and Kaninskii[48,50] proposed a mechanism for the formation of Janovsky reaction products and their decomposition in an acid medium:



It is based on the observation that the acetone residue adds in the keto-form to polynitro-compounds[50] and on the identification of the above decomposition products[48,50]; it may be regarded as the first general mechanism of the Janovsky reaction supported by experimental data. These ideas were confirmed by Foster and Fyfe[84], who, having obtained the Janovsky σ-complex by the interaction of *sym*-TNB with acetone in the presence of tertiary amines, assumed that the amine reacts as a base, after which *sym*-TNB is attacked by the acetone carbanion



However, the same workers showed[85] that in the presence of diethylamine (DEA) the above reaction proceeds via a more complex pathway. After the addition of DEA to an acetone solution of *sym*-TNB, ^{1}H NMR spectra revealed the successive formation of (XL, Y = NEt_2) and then (XXVIIIa), which are converted after a long time into a 1 : 1 mixture of *N*,*N*-diethyl-4-nitroaniline and an aliphatic dinitro-ketone (LVIII). It was established that these compounds are formed directly from (XXVIIIa) in acetone and, when deuterated acetone was used, *N*,*N*-diethyl-4-nitro-[2,6-D]aniline was obtained. A cyclic complex (LIX), which the authors believe is formed either directly from *sym*-TNB or from (LVII) but not via (XXVIIIa), was also isolated from the reaction mixture. On this basis, the authors[85] proposed a general reaction mechanism, which, however, did not receive further experimental confirmation or theoretical justification:



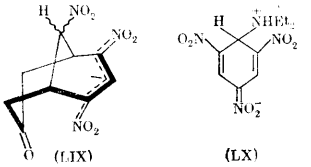
Studies on the kinetics of the reactions of polynitro-compounds with ketones in an alkaline medium have been published comparatively recently. Caldin and coworkers[167] investigated for the first time by the stopped flow method

the kinetics of the reaction of *sym*-TNB with DEA in acetone at low temperatures (down to −85° C). In order to account for the observed third order of the reaction (first with respect to *sym*-TNB and second with respect to DEA), they suggested that equilibrium is established rapidly initially, possibly involving the dimerisation of the amine, which is then followed by the rate-determining bimolecular reaction via the mechanism

$$2DEA + TNB \rightleftharpoons (DEA)_2 + TNB \rightleftharpoons Z \rightleftharpoons TNB.(DEA)_2. \quad (15)$$

(Z is an intermediate complex).

According to the results of a study [168] of the same reaction by the stopped flow method at room temperature, it proceeds in two consecutive stages, the first of which is rapid and reversible (TNB + DEA $\rightleftharpoons$ K) and is of first order with respect to both components. The increase of the concentration of the complex K is found from the increase of absorption at 429 nm. The authors believe that the complex K differs from the charge-transfer complexes Z proposed by Caldin [167] and (LVII) in the mechanism (13) of Foster and Fyfe [55]. The first order with respect to DEA agrees either with the structure of the σ-complex (XL, Y = NEt_2) ($H_2\overset{+}{N}Et_2$ cation) or the zwitterionic complex (LX) formed via the direct interaction between *sym*-TNB and DEA.



(LIX) (LX)

The second, slow stage involves further interaction of the complex K with associated acetone and DEA species, leading to the formation of a complex whose rate of accumulation was determined from its absorption at 516 nm. It is now clear from the work of Strauss [169,170] and Kohashi [98,99] that the final product isolated is the cyclic complex (LIX); similar complexes are formed particularly readily when secondary amines are used as alkaline agents [99,170]. It therefore becomes clear that in all the instances described, involving the use of diethylamine, the authors investigated different processes, predominating under the particular experimental conditions. Caldin [167] probably investigated the kinetics of the first, faster stage of the Janovsky reaction involving both the preliminary formation of the charge-transfer complex (LVII) [mechanism (13)] or Z [mechanism (15)] and the Janovsky complex (XXVIIIa). Although the interaction of *sym*-TNB with acetone in the presence of DEA is not considered in mechanism (15) proposed by the authors, evidently the final product, the rate of formation of which was measured, is in reality a Janovsky σ-complex of type (XXVIIIa). The observed considerable difference between the activation parameters and the orders with respect to DEA of the first rapid stage of the reaction in the studies of Caldin [167] and Osugi [168] is apparently caused by the different contributions of the charge-transfer complex and complex (XXVIIIa) to the measured rate of reaction. At higher temperatures Osugi and Sasaki [168] measured also the rate of the cyclisation reaction (which is not discussed in the present review), leading to the formation of bicyclic compounds of type (LIX) from compound (XXVIIIa) formed initially. The products of the further transformation of the Janovsky σ-complex (XXVIIIa) in an alkaline medium were investigated by Fyfe and Foster [55] [see mechanism (14)].

Features of another type were observed in a study of the kinetics of the interaction of *sym*-TNB and its derivatives with acetone [171] and cyclohexanone [172] in the presence of sodium methoxide. Thus the reaction of *sym*-TNB involves the initial formation of the methoxide σ-complex (XX) together with the Janovsky complex (XXVIIIa). The observed dependence of the initial rate of reaction on the concentration of *sym*-TNB shows that the stage involving attack by the acetonate ion via mechanism (16)–(18) is rate-limiting, and not the acetone deprotonation stage:

$$sym\text{-TNB} + CH_3O^- \xrightarrow{k_1} (XX),\ X = H,\ Y = NO_2\ , \quad (16)$$

$$CH_3COCH_3 + CH_3O^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \bar{C}H_2COCH_3 + CH_3OH\ , \quad (17)$$

$$sym\text{-TNB} + \bar{C}H_2COCH_3 \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} (XXVIIIa)\ . \quad (18)$$

Comparison of the activation parameters of the Janovsky σ-complexes (XXVIIIa) and (XXXIX, X = NO_2) [171,172] with the known characteristics of the Meisenheimer σ-complexes (XX) [174,175] shows that the former are more stable.

According to Kimura et al., [90] the type (XXI, R = X = OMe) σ-complex of 2,4,6-trinitroanisole and methoxide formed initially in an acetone–methanol medium is not solvolysed by acetone to (XXIV, X = OMe), as happens at high concentrations of the complex [83]; this requires an additional amount of methoxide. The change in the rate of generation of the colour as a function of the order in which sodium methoxide and 2,4,6-trinitroanisole are added is associated with the formation of diacetone alcohol from acetone via mechanisms (19) and (20); diacetone alcohol was detected chromatographically in a mixture of acetone and sodium methoxide. Thus the overall mechanism of the complex reactions occurring in the reaction system may be represented by Eqns. (17) and (19)–(21):

$$CH_3C\bar{O}CH_2 + CH_3COCH_3 \rightarrow CH_3COCH_2{-}C(CH_3)_2O^-\ , \quad (19)$$

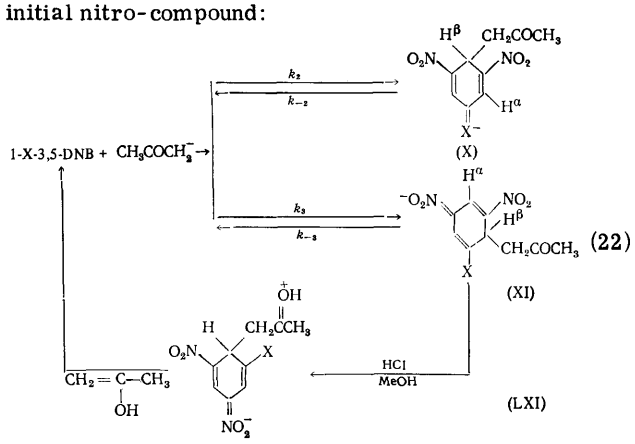
$$CH_3COCH_2C(CH_3)_2O^- + CH_3OH \rightarrow CH_3COCH_2C(CH_3)_2OH + CH_3O^-\ , \quad (20)$$

$$2,4,6\text{-trinitroanisole} + \bar{C}H_2COCH_3 \rightarrow (XXIV),\ X = OMe,\ R = CH_2COCH_3\ . \quad (21)$$

The kinetics of the interaction of *m*-DNB and its derivatives with acetone in an alkaline medium have been studied to an even lesser extent. Gitis and coworkers [175] showed that in aqueous acetone (15% H_2O) complexes of type (VII) are formed via a first-order reaction with respect to *m*-DNB and the alkaline agent. The reaction is faster when the alkaline agent and not *m*-DNB is added last to the solution, which is due to the consumption of alkali in side reactions with acetone. The authors believe that the results support mechanisms (9) and (10).

The kinetics of the formation of complexes by 1-X-3,5-dinitrobenzenes in a mixture with methanol and acetone [62] (X = $COCH_3$, $CONMe_2$, $CONC_5H_{10}$, or $CONH_2$) and cyclohexanone [111] (X = CN, COOMe, or $CONC_5H_{10}$) in the presence of sodium methoxide have been investigated. The authors believe that the reaction proceeds in two stages, the first of which [a reaction of type (17)] is much faster; this ensures a constant ratio of the concentrations of the MeO^- ion and the ketone anion and the first order of the reaction with respect to these components. The rates of formation of both complexes are much higher than the rates of their decomposition and of the isomerisation of the symmetrical isomer (X) to the asymmetric isomer (XI). The latter is independent of the concentration of the methoxide, but increases with the methanol content, which

indicates[62] isomerisation via the decomposition of (XI) to the initial nitro-compound:



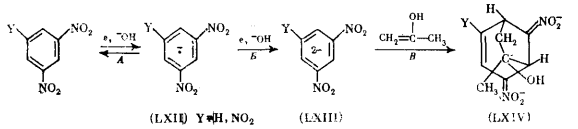
(22)

The quantities k_2 and k_3 increase with decrease of methanol concentration in solution and with increase of the electronegativity of the substituent X. The rate of formation of cyclohexanone complexes (XXXIX)[111] is 50 times greater than the rate of formation of acetone complexes[62]. According to the authors, this is due to the greater acidity of cyclohexanone (the concentration of its anion should be higher by three orders of magnitude). The weakening of nucleophilic properties and steric hindrance to a large extent diminish this effect. The authors[111] believe that acidification of the reaction mixture with HCl solution in methanol leads to the conversion of (XI) into the σ-complex (LXI) protonated at the carbonyl group, which then decomposes to the initial nitro-compound and the enolic form of acetone [reaction (22)].

Thus the kinetic data available at present do not permit unambiguous conclusions about the mechanism of the Janovsky reaction. As a rule, the conditions of the kinetic measurements (mixtures of acetone and other solvents, unusual alkaline agents such as DEA, MeO^-, etc.) are very markedly different from the conditions of the Janovsky reaction and the findings must be used with caution for the interpretation of its mechanism.

One should note that the majority of workers[62,90,167,168,171,175] treat the results of kinetic measurements within the framework of the traditional mechanisms (9)–(10) and (16)–(18). On the other hand, a number of facts have been discovered which do not fit within the framework of these ideas and require a detailed study of the elementary steps. This is, in the first place, the detection of the radical-anions of nitro-compounds in typical activated nucleophilic substitution reactions[176-182], so that a radical chain mechanism has been proposed for these processes[183-188]. The formation of oxygen in the Janovsky reaction, which has been detected polarographically both when an acetone solution of *m*-DNB is acted upon by KOH[189] and in the conversion of the "paired" complex (LII) into the σ-complex (XXVIII) in the presence of acetone and KOH[150], cannot be accounted for by mechanisms of types (9), (10), and (12). This suggests that the Janovsky reaction includes a stage involving electron transfer from the OH^- ion, the electron-donating properties of which are well known[190]. It appears that the evolution of oxygen is due to the decomposition in acetone of the hydrogen peroxide formed from the ȮH radicals after the electron transfer step. Quantitative formation of H_2O_2 in this process has been recently demonstrated experimentally[191,192]. Having observed the broadening of the proton signals of *sym*-TNB and the positive polarisation of the H^β protons of the σ-complex (XXVIII), Beletskaya and coworkers[86,87] do not rule out the possibility of the formation of intermediate radical species in the Janovsky reaction.

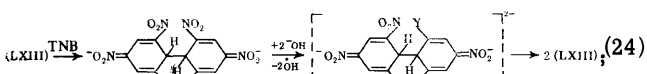
The role of electron transfer and the involvement of individual intermediate species in the elementary steps of the Janovsky reaction have been elucidated with the aid of electrochemical modelling. Polarographic reduction of *m*-DNB derivatives in DMF and acetone[189,193] showed that the reversible electron transfer at the potential of the first half-wave leads to the appearance of the radical-anions (LXII). It is seen from the results[194] of coulometric measurements in a circulation cell[195] that one electron is consumed in the reduction of *m*-DNB to (LXII, Y = H), while the addition of the second electron leads to the formation of the dianion (LXIII, Y = H), which interacts with acetone and gives rise to a doubly charged bicyclic complex with the postulated structure (LXIV, Y = H):



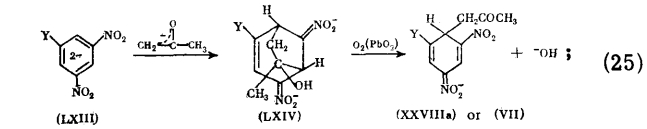
(23)

Coulometric measurements[194] have also shown that the formation of the corresponding intermediate complexes in the reaction of *sym*-TNB—the tentative bicyclic complex (LXIV, Y = NO_2) and the "paired" complex (LII)—also involves the consumption of two electrons; (LII) is then irreversibly reduced and gives rise to two (LXIII, Y = NO_2) species. The bicyclic complex (LXIV), formed on rapid interaction of the dianion (LXIII) with acetone, is fairly stable in an inert atmosphere. Under the influence of oxygen, (LXIV) is converted into the corresponding σ-complexes. Electrolysis at a controlled cathodic potential[194] made it possible to obtain the σ-complexes (VII) and (XXVIIIa), agreeing in terms of all characteristics with the complexes synthesised chemically[50,58].

The set of data obtained suggest[189,193,194] that the Janovsky reaction includes the same stages as the electrochemical reduction of aromatic polynitro-compounds in acetone with the sole difference that the electron donor in the former case is the hydroxide ion. In a general form the mechanism of this reaction may be supplemented, apart from Eqn. (23), by processes (24)–(26). The radical-anions (LXII) are generated in the first stage, some being converted under the influence of oxygen into the initial reactant and others being reduced by OH^- ions to the dianions (LXIII).



(24)



(25)

$$2\,^{-}OH \longrightarrow 2\,\dot{O}H \longrightarrow H_2O_2 \longrightarrow H_2O + \tfrac{1}{2}O_2 \,. \qquad (26)$$

Owing to their high reactivity, they immediately undergo further transformations, attacking the double bond of the enolic form of acetone with formation of the bicyclic complexes (LXIV) via reaction (23). In the presence of an

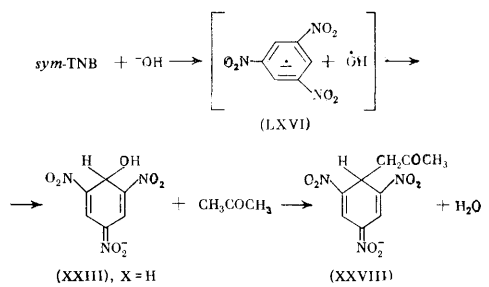
excess of a strong electron acceptor (*sym*-TNB) the interaction of the latter with the dianion (**LXIII**, Y = NO_2) leading to the paired complex (**LII**), is more likely. Under the influence of alkali, the latter is reduced (by the addition of two electrons) to (**LXV**), which dissociates into two dianions (**LXIII**) via mechanism (24). The compound (**LXIV**, Y = H or NO_2) formed subsequently is oxidised by oxygen and converted into the final product of the Janovsky reaction, namely the σ-complex (**VII**) or (**XXVIIIa**) respectively.

The majority of the intermediates indicated in mechanisms (23)–(25) have been identified in solutions in the course of electrochemical simulation or isolated in a free form. The structure of the bicyclic complexes (**LXIV**) was not demonstrated unambiguously [189,194], since, owing to their low stability, they cannot be isolated from the reaction solutions. The available experimental data show that they are doubly charged species; the absorption bands at 688 and 510 nm in the spectra of the reaction solutions have been assigned to (**LXIV**, Y = H) and (**LXIV**, Y = NO_2) respectively, the wavelengths being close to the maxima of the absorption bands of the bicyclic σ-complexes (**LIX**) obtained by Strauss [169,170] from *sym*-TNB. Mechanisms (23) and (25) explain the evolution of oxygen in the Janovsky reaction (26) and confirm the presence of the stage involving electron transfer from the OH^- ion in accordance with Eqn. (23) and subsequent dimerisation of ȮH radicals via mechanism (26).

When alkali is used as the electron donor in acetone solutions, it is not possible to detect the radical-anions of the initial nitro-compounds, because they are "quenched" by the oxygen evolved. This reaction stage was detected [196] by EPR when an acetone solution of *m*-DNB was treated with sodium thiophenoxide as the alkaline agent. Further reactions of the radical-anion formed from *m*-DNB lead, as in the Janovsky reaction with KOH, to the σ-complex (**VII**) as the final product. When potassium 2,4,6-tri-t-butylphenoxide, which has a low oxidation potential (−0.305 V relative to the saturated calomel electrode in DMF), is used as the electron donor in the reaction of acetone with *m*-DNB and *sym*-TNB in a 20 : 1 DMF–acetone mixture in an inert atmosphere, it is possible to detect by EPR the tri-t-butylphenoxy-radical, which is formed from the initial phenoxide as a result of electron transfer. Thus it proved possible in this experiment to detect directly for the first time species formed from the electron donor after the one-electron transfer step. As for the thiophenoxide, the final reaction products in this case are the σ-complexes (**VII**) and (**XXVIIIa**), which have been identified on the basis of their absorption spectra.

Data for the chemical simulation of this process constitute convincing confirmation of the involvement of the *m*-DNB dianion in the intermediate stage of the Janovsky reaction [197,198]. Using the method of homogeneous electron transfer from the dipotassium salt of the cyclo-octatetraene dianion (**LXIII**, Y = H) were obtained in quantitative yields. Experimental data showed that (**LXII**, Y = H) does not react Experimental data showed that (**LXII**, YH) does not react with acetone, a stable EPR signal, identical with that of the radical-anion formed by the electrochemical reduction of *m*-DNB [193] being observed under these conditions. On the other hand, when the *m*-DNB dianion (**LXIII**, Y = H) is treated with acetone, an unstable compound is formed and on contact with oxygen is rapidly converted into the Janovsky σ-complex (**VII**). The latter is formed as a result of the direct interaction of the dianion with acetone, since the σ-complex (**VII**) was not obtained on treating with acetone the *m*-DNB dianion subjected to a preliminary treatment with oxygen. Thus, of the two charged *m*-DNB species, only the dianion (**LXIII**, Y = H) interacts with acetone in the absence of alkali and forms the Janovsky complex (**VII**). Furthermore the product of the interaction of the *m*-DNB dianion with acetone has been converted into the σ-complex (**VII**) in the complete absence of oxygen but in the presence of another electron acceptor—lead dioxide [197]—which constitutes yet another demonstration of the presence of the stage involving the oxidation of the bicyclic product (**LXIV**) into the final σ-complex and of the overall reaction mechanism (23)–(26).

It has also been suggested [199] that the Janovsky reaction may proceed via the hydroxylated σ-complex (**XXIII**, X = H), the formation of which is preceded by electron transfer, the radical-anion of the polynitro-compound reacting with the ȮH radical in the cage (**LXVI**). Under the influence of a large excess of the ketone, this is followed by the displacement of the OH group by the acetone residue and the formation of the Janovsky σ-complex (**XXVIIIa**):



(27)

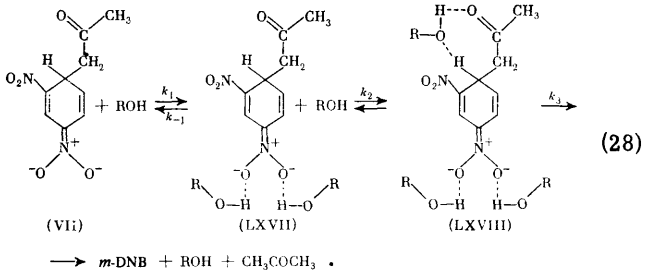
These conclusions are based on the fact that, when alkali is added to a solution of *sym*-DNB and an aromatic compound with activated methyl groups in DMSO, the σ-complex of *sym*-TNB with the OH^- anion of type (**XXIII**) is formed initially and then gradually converted into a complex of type (**XL**) with the above nucleophiles [153,154]. It has also been shown [91,136] that acetone and acetonitrile displace the OH group from σ-complexes of type (**XXIII**), forming more stable complexes of types (**XXVIII**) and (**VII**). A mechanism similar to mechanism (27) was then extended [175] to *m*-DNB in view of the observation that the reaction is of first order with respect to both alkali and *m*-DNB. However, it is noteworthy that the first order of the reaction with respect to KOH is also possible for mechanism (23) if stage (23*A*) or (23*B*) is rate-limiting. On the other hand, the identification of the radical-anions of the polynitro-compounds in the reaction solutions by EPR [176,183,196,200] shows that they emerge from the cage and can participate in other processes, differing from the pathway indicated by mechanism (27).

2. Decomposition of σ-Complexes by Proton-Donating Agents

The overall mechanism of the Janovsky reaction [Eqns. (9) and (10)] shows that the σ-complexes formed in an acid medium decompose to the initial nitro-compounds [48,50]. Whereas the decomposition of the *sym*-TNB complex (**XXVIIIa**) under these conditions requires a fairly concentrated acid, the *m*-DNB σ-complex (**VII**) undergoes slow decomposition [201–205] even in aprotic polar solvents (acetone, DMSO, DMF, etc.). The addition of other polar aprotic solvents (DMSO, DMF, etc.) to the acetone solution does not affect the rate of decomposition of the σ-complex (**VII**), while the introduction of an alcohol or water sharply increases it [201]. When the content of the proton-donating

additive in the mixture is small (up to 4–6 M), the reaction is of first order with respect to both ROH and the complex undergoing decomposition, the second-order rate constants being proportional to the acidity of the alcohols employed.

The addition of large amounts of an alcohol (or water) to acetone leads to a deviation from the linear relation between $\lg k$ and N_{ROH}, which is due to the manifestation of the specific solvation of the complex by the alcohol or water. According to the authors[202], it occurs as a result of the formation of hydrogen bonds involving the nitro-groups, as in (LXVII), and the typical mechanism of the decomposition of σ-complexes of type (VII) by polar proton-donating solvents may be represented by the following scheme:



(28)

One should note that the second nitro-group can also participate in the formation of hydrogen bonds with the solvent. The decomposition is then a second-order reaction, whose rate is determined by the rate of formation of the intermediate complex (LXVIII) ($k_3 \gg k_2$). Together with *m*-DNB, a certain amount of 2,4-dinitrophenylacetone was detected [Eqn. (30)].

At high concentrations of the proton-donating solvent the influence of structure formation in the solvent is superimposed on this process, apart from the solvation effect[202]. The decrease of the rate of decomposition of the σ-complex (VII) for a water mole fraction greater than 0.7 is associated with formation under these conditions of the three-dimensional structure of the framework characteristic of water, which greatly reduces the concentration of "free" H_2O molecules attacking the σ-complex in accordance with mechanism (28).

A change in the composition of the mixed solvent influences not only the rate of decomposition of the σ-complex (VII) but also its optical characteristics (λ_{max} and ϵ_{max}). It has been shown by ^1H NMR[202] that this does not entail the substitution of the acetone residue in (VII) by the conjugate base of the solvent with formation of complexes of the type (XX, X = Y = H).

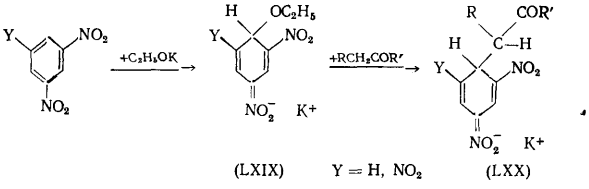
The stability of the σ-complexes of *m*-DNB derivatives increases as the electron-accepting properties of the substituent X are enhanced and the change in the first-rate constant is largely determined by the entropy factor[203,204]. A linear correlation is observed between the values of σ_X for the substituent and the logarithms of the decomposition rate constants[204] for isomers (IV) and (V); the sensitivity constant ρ for the latter isomer is twice as high as for the former. The authors believe that the cyclohexadiene system of the σ-complexes (IV) and (V) has a capacity for transmission of electronic effects close to that of an aromatic structure. Both in the decomposition by water in acetone[203,204] and in the reversible acid-catalysed decomposition in an acetone–methanol medium[62], the rate of decomposition of "symmetrical" isomers of types (V) and (X) is much higher than for the "asymmetric" isomers (IV) and (XI). The decrease of the concentration of methanol and the increase of the electronegativity of X under these conditions lead to an insignificant diminution of the constants k_{-2} and k_{-3} for the decomposition of isomers (X) and (XI) [mechanism (22)], which the authors[62] attribute to a decrease of the degree of solvation of the anion by methanol. On passing from the "acetone" complex (XI, X = $CONC_5H_{10}$)[62] to the analogous cyclohexanone complex[109], the stability of the σ-complex increases appreciably; it is believed that this is due to an additional energetically preferred interaction of the piperidine and cyclohexane rings.

When alkali is added[205] to an aqueous acetone solution of the σ-complex (VII), its decomposition is accelerated sharply. The first order of the reaction with respect to the initial compound and alkali and the dependence of $\lg K_{act}$ on the concentration of the alkaline agent suggested that the main step in the alkaline decomposition is attack by the OH^- ion on the σ-complex (VII).

Thus in the presence of proton-donating solvents, and in an acid medium, Janovsky σ-complexes decompose mainly to the initial compounds owing to solvation by the proton-donating component. On the other hand, the mechanism of the alkaline decomposition of type (VII) complexes still remains unelucidated.

3. Oxidation of σ-Complexes

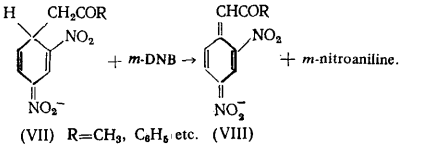
Detailed studies of the behaviour of type (VII) σ-complexes in the reaction system showed that, in the presence of an excess of the polynitro-compound, (VII) may be oxidised. This has been established in connection with the study of the mechanism of the Zimmermann reaction[206], which has been suggested for the analysis of ketosteroids with the aid of *m*-DNB (solvent—alcohol). Foreman et al.[110] initially proposed a reaction mechanism where the polynitro-compound reacts with the alkoxide in the first stage and gives rise to the complex (LXIX), while in the second stage the alcohol is displaced by the ketone with formation of a coloured salt, which has the general structure (LXX):



(29)

However, it was found that in fact the type (LXX) σ-complex is oxidised by the excess of the nitro-compound under the reaction conditions.

The possibility of such oxidation was first suggested by Isidate and Skaguchi[207], who proposed the reaction mechanism



(30)

This course of the reaction in the presence of an excess of the nitro-compound was then demonstrated by numerous investigations[114,208–212]. Mechanism (30) has also been confirmed[209] by the similarity of the absorption spectra of the products of the interaction of acetone or acetophenone with *m*-DNB under the conditions of the Zimmermann reaction and the spectra of 2,4-dinitrophenylacetone or 2,4-dinitrobenzyl ketone in an alkaline medium, which had been

noted earlier[38]. The results of spectrophotometric studies on the Janovsky and Zimmermann reactions are presented in a short review[210].

The agreement of the products of the Zimmermann reaction with structure (VIII) has been demonstrated convincingly by Kimura and coworkers[51,56], who isolated this compound in a free form, determined its structure, and demonstrated its difference from the Janovsky σ-complexes. The authors proposed a general mechanism (31) for the reaction of *m*-DNB in an alkaline medium, which is similar to mechanism (30):

$$m\text{-DNB} + \text{acetone} \xrightarrow{-OH} \text{(VII)} \xrightarrow{\text{oxidation}} \text{(VIII)} \xrightarrow{-OH} \text{unidentified products} \qquad (31)$$

The polarographic reduction potentials of *m*-DNB (−0.62 V), the Janovsky complex (−0.68 V) and the Zimmermann complex (−0.63 V) which they measured[56] (at pH 13) hardly confirm the earlier view[206-209] that *m*-DNB can oxidise (VII) to (VIII). The authors[213] suggest that the oxidation stage is not rate-limiting in the Zimmermann reaction.

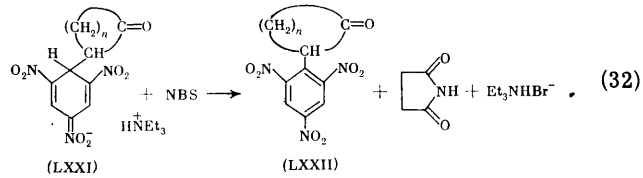
The study of the electrochemical mechanism of the oxidation[214] of Janovsky σ-complexes derived from *m*-DNB and *sym*-TNB showed that they are irreversibly oxidised in a single two-electron stage. Electrochemical oxidation and oxidation by manganese(III) acetate convert the σ-complex (VII) into 2,4-dinitrophenylacetone. The comparatively high oxidation potential of the σ-complex (VII) obtained ($E_{1/2}$ = +0.330 V) shows that a fairly strong oxidant is necessary for the occurrence of the Zimmermann reaction.

Recent quantum-chemical calculations[151] showed that the benzenoid structure, in which the negative charge is distributed principally between the methylene carbon atom (−0.320) and the ring (−0.276), is largely retained in the anion (VIII) of 2,4-dinitrophenylacetone.

Thus it can be regarded as established that the Zimmermann reaction involving *m*-DNB and its derivatives consists in further oxidation of the Janovsky σ-complex by the excess of the nitro-compound with formation of more stable type (VIII) products. The insignificant amount of 2,4-dinitrophenylacetone formed in the decomposition of type (VII) σ-complexes by proton-donating agents [mechanisms (9) and (10)] is apparently due to oxidation by the excess of the *m*-DNB produced. On the other hand, the quantitative yield of the initial *sym*-TNB in the decomposition of its type (XXVIII) σ-complexes shows that reaction (30) does not occur here. This is evidently due to the greater stability of (XXVIIIa), whose oxidation requires a stronger oxidant, in conformity with its higher oxidation potential[214] ($E_{1/2}$ = +0.825 V). Indeed, it has been shown for the oxidation of a number of σ-complexes (XL) by copper(II) oxide[159], chromium oxide[160], *p*-benzoquinone[164], tropylium tetrafluoroborate, and the bromine–pyridine adduct[165] that *sym*-TNB derivatives containing the corresponding aromatic or alicyclic groups in the 1-position are formed in high yields.

There are also other instances of the oxidation of σ-complexes by *sym*-TNB with retention of the added nucleophile. These include the conversion of the trianionic complex (XLVI) on oxidation with bromine into 2-methyl-4,6-dinitrocoumaran[142]. Wennerström and coworkers[162,164] oxidised a mixture of the isomers of (XL, Y = cyclopentadienyl) under mild conditions with *p*-benzoquinone or hydrogen peroxide in an acid medium to a mixture of 2,4,6-trinitrophenylcyclopentadienes and they also oxidised the σ-complex (XLm) or the corresponding nitronic acid (LVIb) to indenyl-2,4,6-trinitrobenzene.

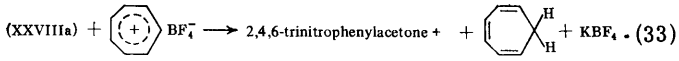
The oxidation of the σ-complexes (LXXI), obtained in an earlier study[119], by *N*-bromosuccinamide in methanol at 0°C has been described[215]:



(LXXI) (LXXII) (32)

This led to the isolation of the ketones (LXXII) in a high yield. The reaction is of a general type and the complexes obtained from cyclopropyl methyl ketone and acetophenone are also readily oxidised to the corresponding trinitrophenyl ketones. The oxidation of asymmetric ketones, capable of giving rise to carbanions of different types, yields a mixture of products.

Many oxidants have been investigated by Kursanov and coworkers[216], who obtained 2,4,6-trinitrophenylacetone in 93% yield by oxidising the σ-complex (XXVIIIa) with tropylium tetrafluoroborate:



(33)

The authors showed that both two-electron (lead tetraacetate, hypohalogenites, and halogens) and one-electron (Fenton's reagent, silver nitrate, and ferric chloride) oxidants may be used, the rate and yield of the reaction depending on the standard potential of the oxidant. 1-Trihalogenomethyl-2,4,6-trinitrobenzenes have been obtained similarly from the σ-complexes (XL, Y = CCl_3, CBr_3, or CI_3) by oxidation with chlorine or bromine in t-butyl alcohol and pyridine.

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