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The α-Effect in the Chemistry of Organic Compounds

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The anomalously high reactivity of compounds with one or several lone electron pairs at the atom adjoining the reaction centre (the α-effect) is discussed in relation to reactions involving nucleophilic substitution at the carbon atom in various valence states. The manifestation of the α-effect is noted for nucleophilic addition to a carbon atom; other examples of the α-effect in the chemistry of organic compounds are quoted. The possible causes of the effect are discussed, and a quantitative estimate of the latter is made.
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I. INTRODUCTION

The report[1] describing the manifestation of the α-effect was published in 1955, but 1962, when Edwards and Pearson[2] first introduced the term "α-effect" and formulated its general characteristics, must be regarded as the date when research on this phenomenon began.

The α-effect is the term given to the anomalously high nucleophilic reactivity of many compounds having one or more pairs of lone electrons at an atom adjoining (i.e. in the α-position) a nucleophilic centre. Such compounds are hydrazine and its derivatives, hydroxylamine, hydroxamic acids, peroxide anions, the hypochlorite ion, etc. Epstein et al.[3] suggested that substances of this type can be referred to as α-nucleophiles and they are sometimes referred to in the literature as hypernucleophiles[4]. The α-effect is manifested as an appreciable positive deviation from the relation described by the Brønsted equation[5-7]:

$$\lg k = \beta pK + C \ .$$

The α-effect continues to attract the unflagging interest of chemists. The lack of a clear-cut understanding of the source of the high reactivity of α-nucleophiles led to numerous studies of reactions of different types, including reactions involving unsaturated and saturated carbon atoms[14-17]. The manifestation of the α-effect at nitrogen, phosphorus, sulphur, and peroxide oxygen atoms is being vigorously investigated[13,17-20]. A few years ago two reviews devoted to the α-effect were published[12,13], but they suffer from significant deficiencies: firstly, the numerous examples of the manifestation of the α-effect in organic chemistry are insufficiently covered, and, secondly, the reviews are somewhat obsolete, difficult to get hold of, and do not include the work of Soviet investigators.

The aim of the present review is to give a systematic account of the experimental observations of the α-effect in various processes in the chemistry of organic compounds, to discuss the possible causes of its manifestation, and to estimate it quantitatively. The review covers the literature up to 1976, that for 1977 is only partly included.

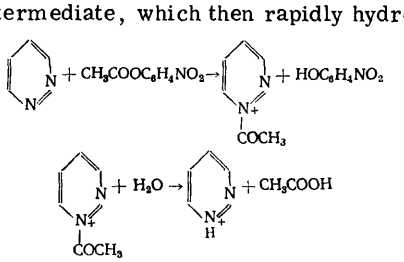
II. MANIFESTATION OF THE α-EFFECT IN THE CHEMISTRY OF ORGANIC COMPOUNDS

1. Nucleophilic Substitution Reactions at a Carbonyl Carbon Atom

Extensive data confirming the manifestation of the α-effect involving nucleophilic substitution reactions at a carbonyl carbon atom have now accumulated. In the reactions discussed below the α-effect has been studied in greatest detail.

(a) Reactions with carboxylate esters. Reactions involving the nucleophilic substitution of carboxylate esters by nucleophiles of different types have been investigated in fair detail; considerable factual data have accumulated concerning the manifestation of the α-effect, particularly in reactions with participation of aryl acetate esters[5,16,17,20-23]. Oximate anions[24] and hydroxamic[26-28] and *trans*-cinnamohydroxamic acid[29] exhibit an anomalously high reactivity in their reactions with 4-nitrophenyl acetate. The α-effect has also been observed in the reactions of 4-nitrophenyl thioloacetate with hydrazine in acetonitrile[30]. Analogous high reactivities have been noted in the interaction of benzohydroxamic acids and their *N*-methyl-substituted derivatives with phenyl acetate in 12% aqueous ethanol[31]. The ClO^- anion reacts with 4-nitrophenyl acetate twice as fast as the hydroxide ion, despite the fact that the latter is 10^9 times more reactive[16].

An anomalous reactivity is shown by certain heteroaromatic nitrogen-containing nucleophiles (pyridazine, phthalazine, and quinoline)[24,32]. Pyridine bases and diazines react with 4-nitrophenol acetate via a mechanism involving nucleophilic catalysis, which consists in the addition of a nucleophile to the substrate with formation of the *N*-acyl intermediate, which then rapidly hydrolyses[33,34]:



In contrast to pyrazine, pyrimidine, and thiazole, pyridazine and isothiazole exhibit the α-effect in the interaction with 2,4-dinitrophenyl acetate[24,32]. The high reactivity of benzohydroxamic acids in reactions with 4-nitrophenyl benzoate and 4-nitrophenyl-4-nitrobenzoate has been demonstrated[35]. The α-effect has been noted in the hydrazinolysis and hydroxylaminolysis of the esters 8-acetoxyquinoline, 6-acetoxyquinoline, and 4-(2-acetoxyphenyl)imidazole[27].

In contrast to the aminolysis of esters[5,11,16,17,21], the reactions of hydrazine derivatives with arenecarboxylate esters are characterised by the absence of a catalytic effect both by a second molecule of the hydrazine derivative and by the reaction products[36-38]. The interaction of hydrazine derivatives with esters is greatly accelerated in the presence of small amounts of added carboxylic acids, amides, and tertiary amines; the rate constants for the reactions are linearly related to the catalyst concentration[37-40].

Table 1. The rate constants k (mole litre^{-1} s^{-1}) for the reactions of nucleophiles with chloroformates (in benzene at 25° C)[47-53].

Nucleophile	pK	Ethyl chloroformate	Phenyl chloroformate
$C_6H_5NH_2$	4.60	0.00374	0.183
$C_6H_5NHNH_2$	5.27	0.175	3.36
$C_6H_5N(C_2H_5)NH_2$	—	—	0.172
$C_6H_5CONHNH_2$	3.05	0.0510	1.33
$C_6H_5CON(CH_3)NH_2$	—	0.00576	0.174
$C_6H_5CSNHNH_2$	5.50	0.00410	0.0749
$C_6H_5CSN(CH_3)NH_2$	7.35	0.000721	0.150
$C_6H_5OCONHNH_2$	2.92	0.00752	0 196
$CH_3CONHNH_2$	3.24	0.0235	0.679
$4\text{-}CH_3C_6H_4SO_2NHNH_2$	1.41	—	0.00529
$4\text{-}CH_3C_6H_4SO_2N(n\text{-}C_3H_7)NH_2$	1.35	—	0.00114
$(CH_3)_2C{=}NO^-$	12.40	8.35	—

(b) Reactions with carboxylic acid anhydrides and chlorides. The study of the kinetics of the reactions of aroylhydrazines with carboxylic acid anhydrides and chlorides in benzene has revealed a high nucleophilic reactivity of aroylhydrazines compared with amines of the same basicity[41-46]. The interaction of acylhydrazines with carboxylic acid anhydride is complicated by the autocatalytic influence of the carboxylic acids evolved during the reaction[42-44]. An exception is the reaction of butyrylhydrazine with succinic acid anhydride; the product of this reaction is quantitatively separated from the reaction mixture and has no catalytic effect[44].

Amidoximes, which are hydrazine derivatives, exhibit the α-effect in reactions with chloroformates (chlorocarbonic acid chlorides) (Table 1), whereas in the reactions of arylamines with chloroformates an anomalous enhancement of nucleophilic reactivity has not been observed[53,54]. The reactions of chloroformates with hydrazine derivatives follow second-order kinetic equations for irreversible processes; the rate constants calculated from these equations remain satisfactorily constant during the process and are independent of the concentrations of the initial reactants[51,52,55-57]. Sulphonic acid hydrazines show a high reactivity in reactions with acryloyl chloride[58].

Separate Brønsted relations have been established for α-nucleophiles (hydrazine, acetylhydrazine, semicarbazide, thiosemicarbazide, hydroxylamine, and methoxyamine), on the one hand, and amines which do not show the α-effect, on the other, in reactions of nitrogen-containing nucleophiles with carbon dioxide[59].

(c) Reactions with carboxylic acids. In the study of the kinetics of the reactions of hydrazine with glacial acetic acid at 25° C, Harris and Stone[60] established that the acylation of hydrazine is much faster than that of amines of similar basicity. The interaction of hydrazine and its substituted derivatives with certain carboxylic acids in oleum takes place via a series of transformations with formation of 2,5-disubstituted derivatives of 1,3,4-oxadiazole[61]; when hydrazine reacts with dibasic carboxylic acids in equimolar proportions, polyoxadiazoles are formed[62]. The condensation reactions of hydrazine and acylhydrazines take place satisfactorily only with aromatic carboxylic acids containing strong electron-accepting substituents (NO_2, COOH, etc.) in the ring[62,63]. The reaction with acids containing electron-donating groups is complicated by the sulphonation of the benzene ring by oleum[64,65].

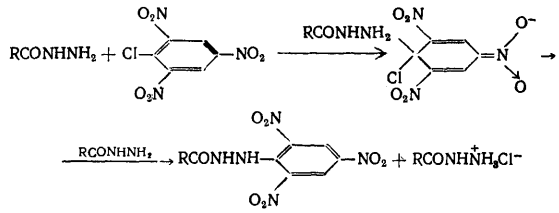
In the condensation of acylhydrazines with carboxylic acids in m-cresol at 120–180° C the rate-determining stage is the slow formation of a cyclic complex between the reactants in the transition state, which decomposes with liberation of water and the formation of the corresponding acyl hydrazine[66-69]. The condensation of diacylhydrazines with dibasic acids takes place similarly and subsequently leads to the formation of polymers[64,65].

2. Nucleophilic Substitution Reactions at a Saturated Carbon Atom

The first report of the α-effect in compounds with saturated carbon atoms is apparently that of Pearson and Edgington[14], who noted that benzyl bromide reacts with the HOO^- anion forty times faster than with HO^-. Benzyl bromide also exhibits a high reactivity in the reaction with neutral forms of amidoximes and N-methylhydroxamic acid[70]. The study of the reactivities of hydrazine, methoxyamine, and a number of different amines in relation to 1-halogeno-2,4-dinitrobenzenes in various solvents showed that hydrazine and methoxyamine exhibit small positive deviations from the Brønsted plot[71-74]. The halogen in 1-halogeno-2,4-dinitrobenzenes is quantitatively substituted by various amines, including α-nucleophiles; in terms of their reactivity, the halogens can be arranged in the sequence F > Cl > Br > I.[71-73] The reactivity of the hydrazine derivative diminishes with enhancement of the electron-accepting properties of the substituent. The same rule holds also in the reactions of picryl chloride with carboxylic and diarylphosphinic acid hydrazides[46,75].

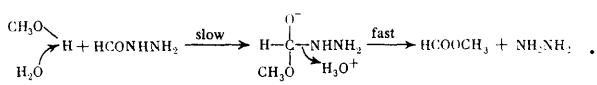
The reactions of acylhydrazines with picryl chloride in benzene follow second-order kinetics. A mechanism has been proposed for the reactions involving the formation in

the slow stage of an addition product (a quinonoid intermediate), which interacts with a second molecule of the initial hydrazine and is converted into the reaction product[76]:

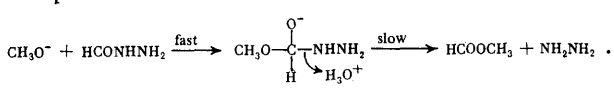


The absence of the α-effect in the reactions of hydrazine and hydroxylamine with alkyl iodides has been firmly established. However, the α-effect is manifested in the reaction of 1,8-naphthyridine with methyl iodide. In this case it is apparently necessary to take into account the geometrical disposition of the diamine heteroatoms (the nitrogen atoms with lone electron pairs are in the *peri*-positions) as a possible cause of the anomalous nucleophilic reactivity of 1,8-naphthyridine[32].

Formylhydrazine is more reactive in methanolysis than amides, which do not exhibit the α-effect[77]. At pH ≤ 5 methanolysis consists in the interaction of the reactants with the rate-determining formation of a tetrahedral intermediate, which then decomposes with the preferential formation of an ester and an amine:



This reaction undergoes general base catalysis. At pH > 9 the methanolysis of formylhydrazine involves the rate-determining decomposition of the intermediate into the reaction products[77]:



An appreciable α-effect has been noted in the reactions of Malachite Green (tetramethyl-4-diaminotriphenylmethane) with hydrazine, methoxyamine, and CN^- and HOO^- ions.

3. Nucleophilic Substitution Reactions at a Phosphorus Atom

Systematic studies on the reactions of phosphate esters have revealed the α-effect for ClO^- and HOO^- ions, hydrazine, and hydroxylamine[82-86]. Isoproyl methylphosphonofluoridate ("Sarin", nerve gas) reacts with the HOO^- ion fifty times faster than with the HO^- ion[86,87-90] despite the fact that their basicity constants differ by a factor of 10^4 (Table 2). It has been noted that hydrazine and hydroxylamine exhibit an anomalous reactivity in the reaction with methyl 4-nitrophenylphosphate[91-93], 4-nitrophenyl phosphate[94], and 2,4-dinitrophenyl methyl phosphate[84,85] anions. The high reactivity of the methyl 4-nitrophenyl phosphate anion in the reactions with hydroxylamine and its *N*-alkyl substituted derivatives supports the occurrence of *O*-substitution and for certain compounds there is a possibility of the formation of a hydrogen bond with the phosphoryl oxygen, which is confirmed by the disappearance of the isotope effect[93].

Hydroximates are nucleophiles with an unusual reactivity in reactions with organophosphorus compounds[86,87,95]. The reactivity of various hydroximates and oximates in reactions with certain organophosphorus anticholinesterases is much higher than has been suggested on the grounds of their basicities[86].

Table 2. The rate constants k(litre mole^{-1} min^{-1}) for the reactions of certain nucleophiles with phosphate esters[85,86].

Nucleophile	p*K*	Zarin	Tetraethyl pyrophosphate	2,4-Dinitrophenyl methyl phosphate
HO^-	15.27	2000	21	0.0505
HOO^-	11.60	94000	2180	10.4
ClO^-	7.4	600	267	—
NH_2OH	6.2	2.6	26	0.053
$C_6H_5CH_2NHO^-$	8.8	1020	160	—

4. Nucleophilic Addition Reactions

(a) Reactions with isocyanates. Nucleophiles can be arranged in the following sequence in terms of the rates of their reactions with isocyanates[96]: $AlkNH_2 > ArNH_2 > AlkOH >$ s-$AlkOH \simeq H_2O > ArOH >$ $RSH > RCOOH$; the position of *N*-substituted hydroxylamines in this series has not been established. It is known that the compounds RNHOH (R = Alk or Ar) react readily with isocyanates via the nitrogen atom, but, with increase of the electronegativity of the substituent, a tendency appears towards simultaneous *N*- and *O*-addition; *N*-substituted hydroxylamines are much more reactive than the corresponding amines in reactions with isocyanates[97]. This is due to the repulsion of the lone electron pairs of the adjacent electronegative atoms in hydroxylamines.

Phenyl isocyanate reacts with hydrazine derivatives in accordance with the following equation[98-109]:

$$R{-}NHNH_2 + O{=}C{=}N{-}R' \rightarrow R{-}NHNHCONH{-}R',$$
$$R = Ar,\ ArCO,\ AlkCO,\ ArSO_2,\ (Ar)_2PO,\ or\ (Ar)_2PS,\ R' = Ar.$$

It has been established that neither the initial reactants nor the products (substituted semicarbazides) influence the rate of reaction of hydrazine derivatives with phenyl isocyanate. The influence of substituents of different electronic types on the reactivity of hydrazine derivatives in reactions with phenyl isocyanate is described by the Hammett–Taft equation. In reactions of phenyl isocyanate with aliphatic acylhydrazines a separate correlation is observed for hydrocarbon groups and hydrogen, on the one hand, and the electronegative substituents, on the other, which is due to the different mechanisms of the effects of these substituents[99].

The enhanced reactivity of hydrazine derivatives in reactions with phenyl isocyanate (Table 3) is associated with the effect of the nitrogen atom of the imino-group adjoining the nucleophilic centre. It is believed that the α-effect in these reactions is due to the appreciable shift of the lone electron pair of the imino-nitrogen in the transition state and that an essential condition for the manifestation of the α-effect is the participation of the hydrogen atom of the imino-group in the formation of a hydrogen bond with the oxygen atom (or another electronegative atom) of the isocyanate[98-102,108]. The lower

reactivity of hydrazine derivatives in reactions with phenyl isothiocyanate is apparently due to the difficulty of the formation of a hydrogen bond of the imino-group hydrogen–sulphur atom type in the transition state[108,109].

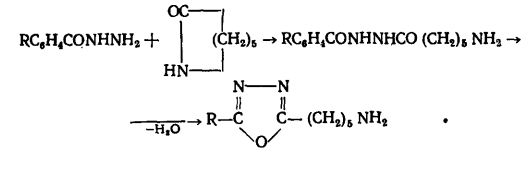
Kinetic studies of the synthesis of urea in the reactions of amines with cyanic acid showed that hydrazine is at least ten times more reactive than was believed on the grounds of its basicity and polarisability[110].

Table 3. The rate constants k (litre mole^{-1} s^{-1}) for the reactions of nucleophiles with phenyl isocyanate and phenyl isothiocyanate (in benzene at 25°C)[50,99-106].

Nucleophile	pK	Phenyl isocyanate	Phenyl isothiocyanate
$(C_6H_5)_2PONHNH_2$	3.02*	0.449	0.000411
$(C_6H_5)_2PON(C_2H_5)NH_2$	2.96*	0.0826	0.000184
$(C_6H_5O)_2PONHNH_2$	2.62*	0.140	0.0000867
$(C_6H_5O)_2PON(C_2H_5)NH_2$	2.51*	0.00534	0.0000203
$(C_6H_5O)_2PSNHNH_2$	2.70*	0.0878	0.0000958
$(C_6H_5O)_2PSN(C_2H_5)NH_2$	2.66*	0.0134	0.0000519
$C_6H_5NH_2$**	4.19*	0.00142	0.0000301
$C_6H_5NHNH_2$	5.27	1.09	—
$C_6H_5CONHNH_2$	3.05	1.92	—
$CH_3CONHNH_2$	3.24	0.614	—
$4\text{-}CH_3CH_4NH_2$**	5.12	0.00386	0.0000843
$4\text{-}CH_3C_6H_4SO_2NHNH_2$	1.41	0.0539	0.000396
$4\text{-}CH_3C_6H_4SO_2N(CH_3)NH_2$	1.36	0.00512	—
$4\text{-}CH_3C_6H_4SO_2N(n\text{-}C_3H_7)NH_2$	1.35	0.00397	—
$C_6H_5SO_2NHNH_2$	1.24	0.0432	—
$C_6H_5OCONHNH_2$	2.92	0.145	—
$C_6H_5N(C_2H_5)NH_2$	5.20	0.00777	—
$C_6H_5N(CH_3)NH_2$	4.99	0.00193	

*Measured in 50% aqueous ethanol.
**Quoted for comparison.

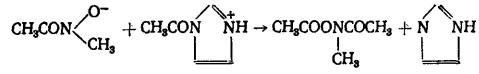
(b) Reactions with ϵ-caprolactam. The reactions of aroylhydrazines with ϵ-caprolactam at 160–270°C in *m*-cresol, decalin, and in the absence of solvents takes place via the following mechanism[111,112]:



The reactions of aroylhydrazines with ϵ-caprolactam in *m*-cresol solution are described by second-order kinetic equations for irreversible processes[111]. The interaction of benzoyl hydrazide, phenylhydrazine, semicarbazide, and carbohydrazide with ϵ-caprolactam in *m*-cresol take place in 10–20 h at 250°C, while in the presence of aniline appreciable changes are not observed even after 100 h.[113] The introduction of small amounts of primary and tertiary amines as well as carboxylic acid derivatives does not affect the rate of reaction of ϵ-caprolactam with benzoylhydrazine, while carboxylic acids themselves, which behave as bifunctional catalysts, accelerate the process[111,112].

5. Other Instances of the Manifestation of the α-Effect

NN-Dialkylhydroxylamines react faster with t-butyl peroxide than do other dialkylamines, which is used in the synthesis of nitrenes[114]. The rate constants for the reactions of hydrazine and hydroxylamine with 4-nitrophenyl sulphate are several times greater than those for the reactions with amines of similar basicity[117]. The α-effect has been observed in the reaction of *N*-acetyl-*N*-methylhydroxylamine with acetylimidazole[115]:



The anomalous reactivity of acetylimidazole in the hydrazinolysis[116-118] and methoxyaminolysis of *N*-acetyltriazole[116] and of 2-acetyl-3,4-dimethylthiazolium iodide in the reaction with hydroxylamine (in contrast to imidazole, which has a similar basicity but is relatively unreactive) has been pointed out[119]. The inapplicability of the Brønsted relation between the logarithm of the reaction rate constant and the basicity/acidity of the catalyst to the acid- and base-catalysed hydrolysis of 4-tolyl *NN*-dimethylacetimidate has been demonstrated[116].

The reactions of δ-thiovalerolactone with hydrazine and morpholine undergo general acid and base catalysis[120]. The hydrazinolysis of δ-thiovalerlactone is much faster than the morpholinolysis of the same thiester, which is due to the α-effect[121].

Two-centre nucleophiles (hydrazine, hydroxylamine, and their derivatives) exhibit an enhanced reactivity in reactions with heterocycles containing polar double bonds (C = X, where X = O, S, N, or P) compared with one-centre nucleophiles (ammonia, primary amines, 1,1-disubstituted hydrazines, and sulphide and hydroxide ions, for example)[122]. The α-effect can have a significant influence on the rate-determining stage of the recyclisation reaction and can affect the mode of the rearrangement; furthermore, two-centre nucleophiles can react via one or two heteroatoms in the ring rearrangement process[122].

The α-effect has been noted in reactions involving the nucleophilic addition of aliphatic 1,1-dinitrocarbanions to methyl acrylate and methyl vinyl ketone in water and 50% aqueous dioxan (the Michael reaction)[123,124]. The virtual equality of the Brønsted β-constants for the addition reactions involving methyl acrylate and methyl vinyl ketone and the recombination of the carbanion with a proton as well as the identical enthalpies of activation for the above reactions indicate the existence of a common stage associated with the localisation of the charge at the carbon atom of the dinitro-carbanion when the hybridisation of this atom changes from sp^2 to sp^3.[124] The rate of the Michael reaction in water at 30°C is 3400 times higher (4200 times higher in 50% aqueous dioxan) for carbanions with R = F than for carbanions with R = CH_3 or C_2H_5, which is apparently due to the repulsion of lone pairs of *p* electrons of the fluorine atom and the carbanion carbon (i.e. the destabilisation of the sp^2-hybridised carbon by the fluorine atom in the α-position)[124].

A series of carbanions derived from *N*-substituted 1,1-dinitroacetamides, i.e. $RNHCOCH(NO_2)_2$, are characterised by an anomalous reactivity in nucleophilic addition to methyl vinyl ketone via the Michael reaction in water and methanol in the temperature range 10–50°C; the operation of the α-effect in these reactions is demonstrated by the authors by the analysis of the influence of various structural factors on the nucleophilic properties in terms of the linear free energy equations[125].

The rate of ferrocenylmethylation of aliphatic 1,1-dinitrocarbanions in 50% aqueous methanol at 45–60°C is independent of the basicity of the anions derived from 1,1-dinitroalkanes [126]. The high rate of ferrocenylmethylation and the absence of *O*-alkylation of dinitro-carbanions are probably due to the influence of the α-effect. The study of the kinetics of the reactions of ferrocenylmethylpyridinium salts with mono- and di-nitro-carbanions permitted a soundly based approach to the selection of the optimum conditions for the preparative synthesis of β-nitro- and $\beta\beta$-dinitro-alkyl derivatives of ferrocene.

The interaction of platinum(II) complexes with hydrazine, hydroxylamine, acid anions, ammonia, and pyridine takes place in two stages; the first stage is slow and rate-determining [127,128]:

$$trans\text{-}[PtL_2Cl_2] + Y \xrightarrow{slow} trans\text{-}[PtL_2ClY] + Cl^-,$$
$$trans\text{-}[PtL_2ClY] + Y \xrightarrow{fast} trans\text{-}[PtL_2Y_2] + Cl^-,$$

where L is an organic ligand, which may be pyridine, piperidine, or $P(C_2H_5)_3$, and Y is a nucleophile. The nucleophilic reaction constants for bivalent platinum in the reactions with hydrazine and hydroxylamine are much higher than in the reactions of the complexes with pyridine, ammonia, and NO_2^- and N_3^- ions; the latter implies that the α-effect is responsible for the much greater reactivity of α-nucleophiles compared with other nitrogen-containing compounds [127,128].

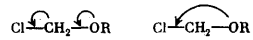
Hydrazine, hydroxylamine, and the HOO^- ion show a much greater reactivity than have been suggested in reactions with the octahedral tris(acetylacetonato)silicon(IV) cation [129]. The high reactivity of such nucleophiles is attributed to the influence of the α-effect, which is manifested by the fact that the lone electron pairs stabilise the transition state, compensating thereby the loss of electrons by the nucleophilic atom [1]:

$$HOO^- + -\overset{|}{\underset{|}{Si}}-X \rightleftharpoons H-\ddot{O}-\ddot{O}-Si-X \quad .$$

The interaction of the reactants is promoted by the high positive charge on the silicon atom and the unfilled outer *d* orbitals of the tris(acetylacetonato)silicon(IV) cation [129]. Sander and Jencks [130] pointed out the extremely high reactivity of the HOO^- ion in its reactions with acetaldehyde and formaldehyde.

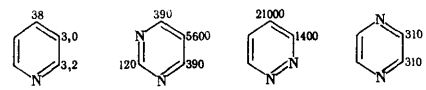
The experimental data on the reactivities of α-carbofunctional compounds of Group IVB elements, the "mesoids" $\diagdown\!\!\overset{|}{\underset{|}{M}}-\overset{|}{\underset{|}{C}}-X$ (where M = Si, Ge, or Sn, i.e. elements having atoms with vacant *d* orbitals; H = Hal, N, O, or S), as well as studies by infrared, NMR, and NQR spectroscopy and other physical methods indicate the anomalous behaviour of the above compounds [131,132]. The ^{35}Cl frequencies in the NQR spectra of mesoids confirm that the mechanism of the transmission of the electronic influences for M = Si, Ge, or Sn differs appreciably from the purely inductive effect for M = C; together with the inductive effect, there is intramolecular coordination between M and X atoms [132]. If M has vacant *d* orbitals, the ^{35}Cl frequency is higher than for the corresponding organic analogue (i.e. for M = C). [133] If M is an atom with lone-pair electrons, then the ^{35}Cl frequency proves to be lower. A more detailed analysis of the NQR spectra of compounds of this type led to the conclusion that the regularity in the variation of the frequencies is associated primarily with the electronegativity of the M atom. The ^{35}Cl NQR spectra of all chloro-derivatives of nitrogen-containing heterocyclic compounds exhibit the above regularity [134]. The appreciably different ^{35}Cl frequencies of the NQR spectra when the chlorine atoms are in the α-positions relative to the nitrogen atoms of the pyridine and pyrrole types in 3-substituted 5-chloro-1,2,4-triazoles are due to the electronegativity of the nitrogen atoms [135].

The high reactivity of the halogen atom (chloromethyl) in alkyl esters compared with the corresponding alkyl halides has been frequently interpreted from the standpoint of the electronic theory. The anomalously low ^{35}Cl frequencies are attributed [136] either to the interaction between the lone electron pair of the oxygen atom and the σ electrons of the C–Cl bond (I) or to the formation of an intramolecular three-centre bond (II):

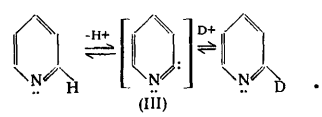


(I) (II)

Zoltewicz et al. [137] demonstrated the non-equality of the rates of isotopic H–D exchange for different positions in the heteroaromatic pyridine, pyrimidine, pyridazine, and pyrazine rings (the numerals indicate the second-order rate constants at 164.6°C, multiplied by 10^6, measured in a CH_3OD-CH_3ONa medium):



Positions which are either adjacent to the nitrogen atom or are located between two nitrogen atoms show the smallest capacity for H–D exchange. The base-catalysed deuterium exchange involving pyridine takes place most readily in the 4-position [138], although, according to calculations of the charges by the Hückel method, the 2-position, should be the most "acid". [137] Calculations by the extended Hückel method show that the 2-carbanion of pyridine is destabilised by the influence of the lone-pair electrons [138]. The loss of stability by the heterocycle is due to the intermediate (or transition) state (III), the formation of which accompanies proton transfer from a position adjoining the nitrogen atom [13]:

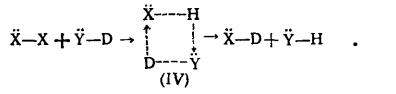


(III)

The reduced reactivity of α-carbon atoms in isotope exchange reactions is the result of the operation of two factors: the decrease of the *s*-character of the hydrogen bond with the carbon atom adjoining the nitrogen atom of the nucleophile and the repulsion between the electron pairs of the nitrogen and the carbanion generated [137,141].

Mention should be made of the α-effect in the exchange of hydrogen for the deuterium of heavy water in ammonia, ammonium salt, and sucrose solutions [142]. The capacity of hydrogen for exchange depends on the nature of the bond; in hydrogen bonds with halogens, oxygen, nitrogen, sulphur, selenium, and other elements having lone-pair electrons the exchange takes place very readily and in many instances instantaneously. The exchange of hydrogen in C–H bonds is as a rule very difficult and may be accelerated only in the presence of strong bases, which promote the abstraction of a proton, in the presence of strong acids, which facilitate the transfer of deuterium, or, finally, in the presence of suitable substituents which weaken the C–H bond. Deuterium exchange takes place

in the reaction complex (IV) formed via hydrogen bonding (Ẍ and Ÿ are atoms or parts of molecules):



(IV)

The maximum rate of the alkaline hydrolysis of the haloforms CHX_3 (X = Hal) is a phenomenon common to all halogenomethanes [143,144]. For example, the rate of hydrolysis of $CHCl_3$ is one thousand times higher than that of CH_2Cl_2 and the rate of hydrolysis of bromine-containing haloforms is higher by approximately three orders of magnitude compared with CH_2ClBr or CH_2Br_2. Carbenes are intermediates in the alkaline hydrolysis of haloforms; 1,1-elimination takes place via the mechanism involving unimolecular elimination from the conjugate base:

$$CHX_3 + HO^- \rightleftarrows CX_3^- + H_2O \quad ,$$
$$CX_3^- \rightleftarrows :CX_2 + X^- \quad ,$$
$$:CX_2 + H_2O \xrightarrow{HO^-} CO + HCOO^- + X^- \quad .$$

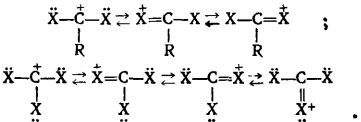
The introduction of a fluorine atom into the haloform has the most appreciable kinetic effect compared with other halogens. Difluoromethanes (CHF_2Cl, CHF_2Br, CHF_2) are hydrolysed much faster, which conflicts with the suggested mechanism. Hine [143-145] interprets these results on the hypothesis of a single-stage bimolecular 1,1-elimination mechanism:

$$HO^- + H{-}CF_2X \rightarrow H_2O + CF_2 + X^- \quad ,$$
$$CF_2 + H_2O \xrightarrow{HO^-} CO + HCOO^- + F^- \quad .$$

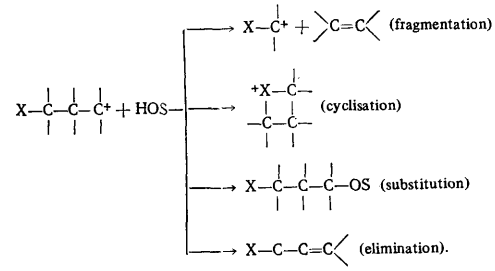
The electron shift from the heteroatom to the electron-deficient carbene carbon has a significant influence on the reactivity of carbenes containing α-heteroatoms with lone-pair electrons. If the heteroatom is linked by a double bond to the carbene carbon, then the shift of electron density leads to the formation of stable compounds such as isonitriles and derivatives of fulminic acid and carbon monoxide [145]; these compounds do not exhibit electrophilic properties and behave as more or less reactive nucleophiles. The carbene ions are stabilised by the lone-pair electrons of the heteroatom X in the α-position relative to the cationic centre [46-148]:

$$R_2\overset{+}{C}{-}\ddot{X} \rightleftarrows R_2C{=}\overset{+}{X}, \quad X{=}Hal,\ N,\ O,\ S,\ or\ Se \quad .$$

The stabilising effect increases sharply if the electron-deficient carbon atom is linked to two or even three electron-donating heteroatoms X [147]:



The stability of the carbonium ion formed in the solvolysis of precursor carbonium ions is exceptionally high in those cases where the atom adjoining the carbonium centre has lone-pair electrons, the symmetry of the orbitals of which is favourable for overlapping with the vacant p orbital of the carbonium centre. Solvolysis of carbonium ions containing α-substituents with lone-pair electrons is accompanied by mutually competing reactions [149,150] (HOS is the solvent):



III. DEPENDENCE ON THE NATURE OF THE REACTANTS

Since the dependence of the α-effect on the nature of the reactants has been analysed in detail in a review [13], in this section we shall consider examples where the α-effect loses its force (vanishes). Epstein et al. [3] suggested a close relation between the manifestation of the α-effect and the nature of the nucleophile and the substrate involved in the reaction. Together with the above examples of the reactions where the α-effect has been noted for hydrazine and its derivatives, data have been obtained on reactions in which hydrazine does not show an enhanced reactivity [151, 152]. Thus, whereas the α-effect is possible in the interaction of 4-nitrophenyl acetate with hydrazine and methylhydrazine, *NN*-dimethylhydrazine does not exhibit a high reactivity; the point corresponding to the above nucleophile fits on the linear Brønsted plot for primary and secondary amines [8].

The α-effect has been demonstrated for reactions of hydrazine, hydroxylamine, sulphides, and other nucleophiles with methyl iodide in methanol [126]; on the other hand, an anomalous reactivity of this substrate has not been observed in the interaction with hydrazine, hydroxylamine, and their monomethyl derivatives in an aqueous medium [15]. Gregory and Bruice's paper [15] was perhaps the first report on the α-effect in the reaction of neutral nucleophiles with saturated substrates. The α-effect has not been observed in the reactions of alkyl iodides with hydrazine in acetonitrile [152], methyl iodide does not exhibit an enhanced reactivity in reactions with heteroaromatic nitrogen-containing nucleophiles (including pyridines, diazines, and their analogues) in dimethyl sulphoxide at 23° C. [32] Hydrazine and methoxyamine react with 1-chloro-2,4-dinitrobenzene, showing very insignificant α-effects [71].

Systematic studies on the nucleophilic reactions of phosphate esters revealed the α-effect for hydrazine and hydroxylamine [84,85]. However, there is no α-effect in the reactions of the monoanion of 4-nitrophenyl methylphosphonate with hydrazine; other nucleophiles show a very insignificant α-effect in their reactions with this substrate [91-93]. The differences between the reactivity of hydrazine, which behaves as a neutral reactant in these processes, and those of other α-nucleophiles are extremely insignificant [88]; the α-effect has not been noted in the hydrazinolysis of phosphate esters [94].

α-Nucleophiles incapable of participating in the formation of a transition state characteristic of the push-pull mechanism have the "normal" reactivity [8,16,153]. Certain amidoximes react very slowly with Sarin and di-isopropyl phosphorofluoridate; *N*-triphenylmethylhydroxylamine

does not react with these substrates at all[154]. The α-effect has not been observed in the interaction of nitroethane with hydrazine, methylhydrazine, hydroxylamine[151], and alkyl iodides[32,153]; this demonstrates in the first place, a close relation between the α-effect and the type of transition state (more precisely Brønsted's β constant). By analogy with proton transfer reactions[15,155], the high values of β should be attributed largely to the intense bond formation in the transition state. However, according to Hammond's postulate[156], this analogy is not altogether correct.

There is no α-effect in the reactions of *NN*-dimethylhydrazine with 2-phenyl-L-4-benzyloxazolone[10], which can be accounted for by the impossibility of the formation of a hydrogen bond with the carbonyl oxygen.

In the deprotonation of t-butylmalononitrile all nucleophiles (including hydrazine, hydroxylamine, methoxyamine, and peroxide ions) show the "normal" reactivity and fit on a single common Brønsted linear plot[155,157]. The α-effect has not been noted in the reaction of 1-chloro-2,4-dinitrobenzene with hydrazine and methoxyamine[46] and of picryl chloride with carboxylic acid hydrazides[50], *N*-alkyl-*N*-arylhydrazines[50], and phosphorus acid hydrazides and their *N*-ethyl-substituted derivatives[104].

The cause of the absence of the α-effect in the reactions of 2,4-dinitrophenyl acetate with pyridine and pyridazine at 25°C in water is not clear[5,33,158]. This example is particularly surprising, since strong interaction of the unpaired electrons of the two nitrogen atoms in the above nucleophiles has been demonstrated and confirmed by molecular orbital calculations[159] and photoelectron spectra[160].

The above example makes it clear that the α-effect depends both on the type of substrate and on the nature of the nucleophile. Fairly convincing experimental data have now accumulated, showing that the α-effect of the substrate depends primarily on the valence state of the carbon atom and can be arranged in the following sequence: $sp > sp^2 > sp^3$. This behaviour is illustrated quantitatively by the ratios k_{HOO^-}/k_{HO^-} and the rate constants for the reactions with bromophenylacetic acid, 4-nitrophenyl acetate, and benzonitrile, which indicate different values of the α-effect due to the carbon atoms in different valence states[161]. It is suggested that the α-effect of the carbon atom is enhanced with increasing *s*-character of the bonding orbitals[152].

IV. THE POSSIBLE CAUSES OF THE α-EFFECT

The possible causes of the α-effect have now been established and analysed[8,128], the main ones being as follows: destabilisation of the ground state of the nucleophile due to the electrostatic repulsion between the electrons of adjacent electronegative atoms[32,162]; stabilisation of the transition state owing to the overlapping of the lone-pair electron orbitals[12,13]; reduced solvation of α-nucleophiles compared with reactants which do not exhibit the α-effect[15,163,164]; stabilisation of the reaction products (this factor also stabilises the transition state[79,115,165]); polarisability of the transition state[163]. During recent years several new causes of the α-effect have been added to the above list[4]. Certain probable causes of the α-effect are discussed in detail below, but any one of them in isolation does not fully account for the nature of this phenomenon.

1. Destabilisation of the Ground State

The first hypothesis of the destabilisation of the ground state of the nucleophile as a possible cause of the anomalous reactivity was put forward as early as 1962.[162] The α-effect in hydrazine derivatives may be due to the difference between the free energies of the ground states of the initial reactants and the reaction products[32,79,166]. The energy of the ground state increases owing to the electrostatic repulsion between the electrons of adjacent electronegative atoms[8,162]. This conclusion is confirmed by the photoelectron and EPR spectra of substituted hydrazines[167-170]. The repulsion of the lone-pair electrons in molecules of the type H_2O_2, NH_2NH_2, HClO, and ClF[171-174] introduces serious errors into estimates of the enthalpies of reaction and heats of dissociation of the adducts of Lewis acids and bases by the Drago–Wayland equation and leads to values of these quantities which are appreciably too low[175,176]. The repulsion of the electron pairs is responsible for the inaccurate prediction of the bond lengths and heats of formation of α-nucleophiles; the calculated bond lengths are too small and the heats of formation evaluated from the incorrect bond lengths are negative[177].

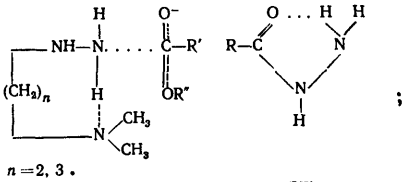
The increase of the energy of the ground state acts in the same direction as the decrease of the activation energy, which leads to an increase of the rate constants; however, the repulsion of the lone-pair electrons should also lead to an increase of basicity. The simultaneous increase of the rate constants and basicity should not apparently result in the appreciable lack of correspondence between basicity and reactivity observed experimentally[8]. In hydrazine and its derivatives the electrostatic repulsion between the lone-pair electrons of the nitrogen atoms diminishes in the transition state owing to the decrease of the charge of the nitrogen atom of the amino-group, the lone-pair electrons of which are involved in conjugation with the bond being formed, stabilising thereby the transition state[178,179]. Furthermore, such conjugation is the cause of the increase of the ability of the NH bridge group in monosubstituted hydrazines to transmit electronic influences in reactions with carbonyl-containing substrates ($z_{NH} \simeq 1$).[51,99,104] The low N–X, O–X, and F–X bond energies are attributed to the influence of the repulsion of the lone-pair electrons in the ground state (X is an electronegative atom), the weakening of the above bonds becoming more pronounced with increase of the electronegativity of X.[180]

2. Stabilisation of the Transition State

The stabilisation of the transition state may be due to general intramolecular base catalysis and resonance interaction. Epstein et al.[3] proposed acid–base mechanisms for reactions involving nucleophilic attack on esters (particularly with formation of hydrogen bonds); similar mechanisms are discussed in later communications[158,182,183]. Bifunctional catalysis and resonance stabilisation have been examined by Jencks[158].

(a) General intramolecular base catalysis. The rate constants for the reactions of 2-dimethylaminoethylhydrazine and 3-dimethylaminopropylhydrazine with phenyl acetate are one thousand times higher than would be expected on the grounds of their basicity[184]. The

high reactivity of dimethylaminoalkylhydrazines is due to the general intramolecular base catalysis [see formula (V)]:



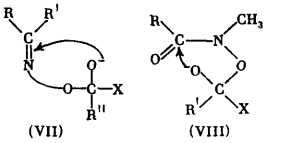
$n = 2, 3$.

(V) (VI)

The occurrence of the catalysis illustrated by formula (V) is confirmed by the dependence of the rate constants on the concentration of the dimethylamino-group in the form of the free base[184].

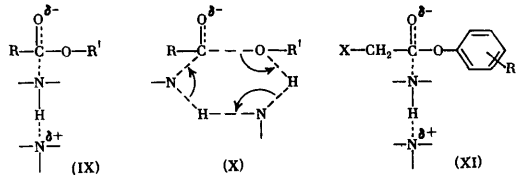
The increased reactivity of carboxylic acid hydrazides in reactions with carbonyl-containing substrates can be explained by general intramolecular base catalysis involving the formation of an intramolecular hydrogen bond of type (VI). The formation of such intramolecular bonds is indicated by the shift of the ν(C=O) and ν(N–H) stretching vibration frequencies in the infrared spectra of carboxylic acid hydrazides[185,186], the measured dipole moments[187], and the study of the structure of the hydrazide group by the CNDO/2 method[188]. The replacement of the oxygen atom of the carbonyl group by the less electronegative sulphur atom leads, on the one hand, to an increased basicity of the amino-group and, on the other hand, to a decrease of the mobility of the hydrogen atoms of the amino-group, which hinders the formation of an intramolecular hydrogen bond; the latter is the most likely cause of the reduced reactivity of thiobenzoylhydrazine[32,48]. Phenoxycarbonylhydrazine, in which an intramolecular hydrogen bond of type (VI) has not been observed[185], exhibits a much lower reactivity compared with benzoylhydrazine despite the similarity of their basicity constants[48,99]. Evidently general intramolecular base catalysis has some effect on the reactivity of hydrazine and its derivatives. However, on the basis of this hypothesis, it is impossible to explain the lower reactivity of *N*-benzoyl-*N*-methylhydrazine in the reactions with ethyl chloroformate[48], phenyl chloroformate[50–52,55], and esters[38] as well as the absence of an increase in the reactivity of hydrazine derivatives in reactions with picryl chloride[46,75]; general intramolecular base catalysis should operate in the above reactions, because the presence of *N*-methyl groups does not apparently affect its occurrence[184].

The manifestation of the α-effect in the acylation of neutral amidoximes[57] and oximate anions with 4-nitrophenyl acetate (VII) can be accounted for by general intramolecular base catalysis[9]. The α-effect in *N*-methylhydroxamic acids has been explained by a similar mechanism (VIII):[189]



(VII) (VIII)

Bruice et al.[183] showed that the aminolysis of esters can also involve general base catalysis (IX–XI):



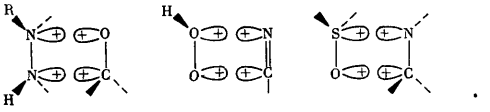
(IX) (X) (XI)

The delocalisation of the negative δ-charge on the carbonyl oxygen atom corresponds to scheme (IX), a cyclic proton transfer corresponds to scheme (X), and the localisation of the δ-charge on the phenolic oxygen atom corresponds to scheme (XI).

The high reactivity of hydrazine in reactions with the esters 4-(2-acetoxyphenyl)imidazole, 6-acetoxyquinoline, and 8-acetoxyquinoline is due to the fact that the adjoining imidazole group promotes a high rate of reaction of the reactants, behaving as a general intramolecular base catalyst; under the same conditions, phenyl acetate reacts with hydrazine forty times more slowly than with 6-acetoxyquinoline[27].

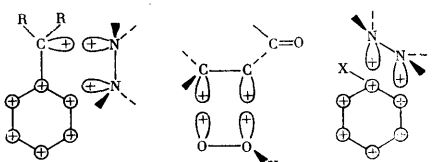
(b) The formation of an aromatic transition state. Liebman and Pollack[190] proposed an explanation of the α-effect based on allowance for the interaction of the electron pair orbitals in the transition state, which does not occur either in the initial reactants or in the products. This interpretation of the α-effect takes into account the fact that a high reactivity is observed only for substrates with π orbitals and provides a much better interpretation of the increase of reactivity than could be achieved by analysing the stability of the reaction products.

By means of this approach, it has been shown that the addition of hydrazine to the carbonyl group leads to the formation of a six-electron aromatic transition state (XII); a transition state of an analogous type is probably formed as a result of the addition of the peroxide ion to benzonitrile (XIII) and of bisulphite to oximes (XIV)[177]:



(XII) (XIII) (XIV)

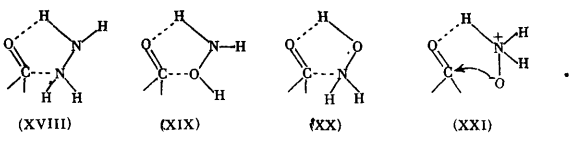
The α-effect in reactions involving the addition of α-nucleophiles to Malachite Green[78,79] can be explained by the formation in the course of the reaction of a cyclic transition state with aromatic properties. If Malachite Green is regarded as a substituted benzyl cation, then (XV) can be treated as a transition state incorporating ten electrons, as a result of which the system acquires aromatic properties[190]:



(XV) (XVI) (XVII)

The addition of peroxide ions in the Michael reaction[121,122] and the transition states in aromatic nucleophilic substitution reactions are illustrated in structures (XVI) and (XVII)[190].

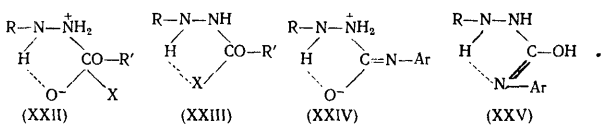
Hydrazine and its derivatives are capable of bifunctional (electrophilic-nucleophilic) interaction with carbonyl-containing substrates (esters, acid halides, acylureas, anhydrides, and oxazolinone). The transition states in the above reactions are illustrated by scheme (XVIII)–(XXI)[10]:



(XVIII) (XIX) (XX) (XXI)

The reaction of oxazolinone with hydroxylamine involves competition between the oxygen and nitrogen atoms in which there is a bifunctional attack on the neutral hydroxylamine molecule [(XIX)–(XX)]. In addition one cannot rule out the possibility of attack by the oxygen atom in the form of the zwitter-ion (XXI); the last scheme explains the formation of a considerable amount of *O*-acyloxazolinone[10]. Epstein et al.[89] describe the appearance of stable transition states in the reactions of Sarin and the ClO^- ion with various phosphorus-containing substrates.

An aromatic transition state in the reactions of monosubstituted hydrazines with carbonyl-containing substrates is formed via a hydrogen bond between the oxygen atom (or another electronegative atom) and the hydrogen atom of the imino-group and via a new bond between a carbon atom of the substrate and the amino-group of the nucleophile. The transition state is of type (XXII) for reactions of monosubstituted hydrazines, of type (XXIII) for reactions with benzoyl chloride[41,50], phenyl chloroformate[51,52], and carboxylate esters[38], and of types (XXIV) and (XXV) for reactions with phenyl isocyanate[99,100]:



The formation of structures (XXII)–(XXV) is favoured by the disposition in a single plane of the hydrogen atom of the imino-group and the lone-pair electrons of the amino-nitrogen[191]. Furthermore, the aromatic transition state promotes a more complete shift of electron pair from the nucleophilic centre and is energetically the most favourable[190,192]. Convincing arguments involving cross-correlation analysis have been put forward for the possibility of the formation of transition states of types (XXII) and (XXIII) in the acylation of carboxylic acid hydrazides by aryl chloroformates and aroyl chlorides[41,52,55].

The hypothesis of the formation of transition states of type (XXII)–(XXV) in reactions of monosubstituted hydrazines with carbonyl-containing substrates is also supported by the kinetic parameters of the reactions with *NN*-disubstituted hydrazines. The replacement of a hydrogen atom in the imino-group by an alkyl substituent eliminates the possibility of the formation of an aromatic transition state, which leads to a decrease of the reactivity of *NN*-disubstituted hydrazines[50,104]. It is clear from the foregoing that, when monosubstituted hydrazines react with carbonyl-containing substrates, there is a possibility of the formation of transition states (XXII)–(XXV) with a high stability. Consequently the α-effect is shown by hydrazine derivatives on interaction with substrates containing π orbitals; the transition states in these reactions are aromatic and contain $4n + 2$ electrons.

By virtue of the specific features of the nucleophilic substitution at an aromatic carbon atom, the formation of transition states (XXII)–(XXV) is impossible in reactions with picryl chloride; the mechanism of such reactions involves the formation of intermediates having quinonoid structures[75]. Presumably this factor is the main cause of the low reactivity of hydrazine derivatives in reactions with picryl chloride.

3. Differences in Solvation Effects

Solvation is not one of the main causes of the α-effect, but the accumulated factual data do not allow neglect of this factor[165,193,194]. It is suggested that α-nucleophiles are much less solvated than other nucleophiles, which do not show the α-effect. This question has not been completely worked out in detail, the interpretation of certain solvation effects still does not fit satisfactorily within the framework of generally accepted theories, and experimental results are difficult to account for in many instances. Furthermore, solvation is one of the destabilising factors which should alter both the basicity and the nucleophilic reactivity of the compound[158]. The nucleophilic properties of hydrazine in acetonitrile in the reaction with 4-nitrophenyl acetate, for example, are much more marked than would follow from the pK value and this is why in an aprotic solvent, such as acetonitrile, hydrazine exhibits the α-effect[15].

Benzamidine (pK = 11.6) reacts with 4-nitrophenyl acetate in chlorobenzene approximately 15 000 times faster than does n-butylamine (pK = 10.6) despite the small differences between the basicity constants[192]. In a study of the reactions of peroxide ions with benzonitriles, Wiberg[163] stated that the HOO^- ion is approximately 10^4 times more reactive than the HO^- ion. The differences between the reactivities cannot be attributed to the low enthalpies of activation and differences between the entropies of activation; this fact should probably be explained by the influence of the solvent (a 50% aqueous acetone solution was used). The reactions of peroxide ions with benzonitriles, which have been studied in detail[161,195], are greatly influenced by solvation[196].

Table 4. The rate constants k (litre mole^{-1} s^{-1}) for the reactions of phenyl isocyanate with certain nucleophiles in various solvents at 25° C[102,103,107] (*DN* is the donor number of the solvent[198]).

Solvent	*DN*	Diphenylphosphinic acid hydrazide	4-Tosylhydrazine	4-Toluidine
Hexamethylphosphoramide	38.8	—	—	0.436
Pyridine	33.1	8.84	—	—
Diethylacetamide	32.2	7.11	—	—
Dimethyl sulphoxide	29.8	7.24	3.57	0.164
Dimethylacetamide	27.8	5.50	1.88	0.0784
Dimethylformamide	26.6	4.90	1.64	0.0601
Tetrahydrofuran	—	3.00	1.25	—
Dioxan	—	2.74	0.923	—
Diethyl ether	19.2	2.63	0.723	0.0347
Ethyl acetate	17.1	2.14	—	0.0315
Methyl acetate	16.5	2.07	—	—
Acetonitrile	14.1	1.72	—	—
Nitrobenzene	4.4	0.727	0.163	0.00697
Benzene	0	0.449	0.0539	0.00397

A parallel relation between the logarithms of the rate constants and the donor numbers (*DN*) of the solvents (Table 4), described by Eqn. (1) for reactions with diphenylphosphinic acid hydrazide[197] and by Eqn. (2) for reactions with tosylhydrazine[103,199], has been demonstrated for the reactions of phenyl isocyanate with certain hydrazine derivatives:

$$\lg k = -0.294 + 0.0372\,DN \quad (r = 0.997), \qquad (1)$$

$$\lg k = -1.12 + 0.049\,DN \quad (r = 0.989)\ . \qquad (2)$$

For the reactions of phenyl isocyanate with 4-toluidine (which does not exhibit the α-effect), the influence of solvents on the reactivity of nucleophiles should be described by the following equation:

$$\lg k = -2.67 + 0.050\,DN \quad (r = 0.987) \quad . \qquad (3)$$

The study of the influence of donor solvents in a mixture with benzene on the rate of reaction of phenyl isocyanate with hydrazine derivatives showed that even small amounts of added donor solvents increase significantly the rate of reaction. A linear relation, described by Eqn. (4) for diphenylphosphinic acid hydrazide [197] and by Eqn. (5) for tosylhydrazine [103], holds between the logarithms of the catalytic rate constants and the donor numbers of the solvents:

$$\lg k = -0.577 + 0.0725\,DN \quad (r = 0.996), \qquad (4)$$

$$\lg k = -1.91 + 0.106\,DN \quad (r = 0.997). \qquad (5)$$

Donor solvents solvate the initial hydrazine, the transition state, and the substrate. The catalytic activities of dimethylformamide, dioxan, and pyridine in reactions of tosylhydrazine and diphenylphosphinic acid hydrazide with phenyl isocyanate and picryl chloride show that the solvation of the substrate does not play a significant role; the different influences of the above solvents are probably a result of the solvation of either the transition state or the initial hydrazine. The approximately same efficiencies of catalysis by donor solvents in reactions of diphenylphosphinic acid hydrazide with phenyl isocyanate and picryl chloride as well as the absence of catalysis in the reactions of *N*-ethyl-*N*-diphenylphosphinylhydrazine and *N*-methyl-*N*-tosylhydrazine [103,197] confirm quite convincingly that solvation involves the hydrogen atom of the imino-group in the initial hydrazide. Consequently the influence of donor solvents in reactions of phenyl isocyanate with phosphorus acid hydrazides and sulphonic acid hydrazides, which leads to an increase of the rate, is most probably associated with the specific solvation of the transition states in these reactions. The effectiveness of the catalysis by donor solvents depends both on the structure of the nucleophile and on the type of substrate employed [197,199].

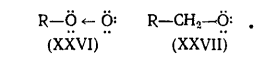
4. Stabilisation of the Reaction Products

The parallel variation of the thermodynamic stability of the reaction products and the deviations from the reactivity–basicity relation have been demonstrated for the interactions of 4-nitrophenyl acetate with alcohols, peroxides, amines, hydrazines, and hydroxylamines [78]. However, the observed deviations show that this type of correlation is not general, particularly when the reactivities of different atoms are compared. The thermodynamics of the stabilisation of the reaction products is important in the interaction of hydrazine and methoxyamine with the carbonium ion of Malachite Green [79,164]. It has been recognised that factors promoting the stabilisation of the reaction products stabilise also the transition state [8,79,80,200–202].

5. Orbital Splitting

The high reactivity of nucleophiles with a lone electron pair at the α-atom can be explained [4,202] in terms of the theories of reactions controlled by the charge and the disposition of the boundary molecular orbitals of the reactants, i.e. the highest occupied orbital (HOMO) and the lowest unoccupied orbital (LUMO). The free energy of the reaction between a nucleophile and a substrate is determined by an equation whose first term describes the electrostatic interaction of the charges of the reactants in the course of the reaction and the second describes the formation of a covalent bond in the transition state [203]. The use of this equation in the study of the interaction of the ClO^- and HO^- ions with the same substrate permitted the conclusion that the former is more nucleophilic despite its lower basicity constant; the theoretical postulates have been confirmed by experimental data [4].

The lone-pair electrons in hydrazine, hydroxylamine, disulphides, and the ClO^- ions are oriented, relative to the electron pair interacting with the electrophile to form a covalent bond, in a manner which leads to the splitting of the orbitals [9,203]. Such splitting can be detected in photoelectron spectra [205,206]. The splitting of the orbitals increases the HOMO orbital energy, which affects the physical properties of the α-nucleophile: the ionisation potential, the redox potential, and the polarisability [9,207,208]. The occupied π^* orbital interacts more strongly with the "electronic" σ^* orbital compared with the unperturbed π orbitals of the usual nucleophiles; there is then a possibility not only of allowed $\pi \rightarrow \pi^*$ transitions but also of transitions of the type $\pi^* \rightarrow \sigma^*$ (Fig. 1). The latter factor is responsible for the increased reactivity [4,209]. The atom adjoining the lone-pair electrons in (XXVI) is more electronegative than the carbon or hydrogen atom in (XXVII), giving rise as a result to a positive inductive effect and reducing thereby the charge on the nucleophilic atom [5,209]. All these factors reduce the extent of the interaction with the approaching substrate:



(XXVI) (XXVII)

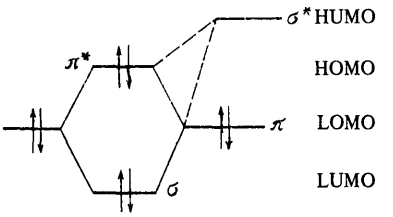


Figure 1. Energy levels of the molecular orbitals of α-nucleophiles: HUMO—highest unoccupied molecular orbital; HOMO—highest occupied molecular orbital; LOMO—lowest occupied molecular orbital; LUMO—lowest unoccupied molecular orbital.

In such cases the change in nucleophilic properties opposes the effect of the change in pK; indeed the CH_3COO^- ion is $10^{4.5}$ times more basic than the $CH_3CH_2O^-$ ion [5], while H_2O_2 is 10^4 times stronger as an acid than H_2O. [209]

Comparison of the energy levels of the ClO^- and HO^- ions shows that in the ClO^- ion there is interaction between the p,π orbitals of the oxygen and chlorine atoms, resulting in the splitting of the energy levels (Fig. 2). Because of this, the HUMO level in the ClO^- ion lies far above the corresponding energy level in the HO^- ion [4]. Fig. 2 shows that the ClO^- ion requires a smaller expenditure of energy ($\Delta E_1 > \Delta E_2$) and is therefore more reactive than the HO^- ion. The intermediate thus produced is

stabilised by a three-orbital covalent bond and its loosening and dissociation are considerably hindered owing to the absence of an effect by the approaching group. The validity of the above treatment is confirmed by the fact that the α-effect is shown by nucleophiles with partial overlapping of the lone electron pair orbitals[4].

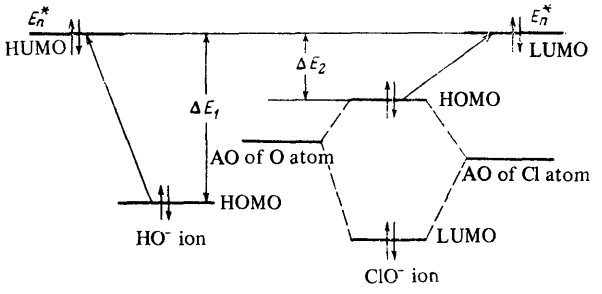


Figure 2. Diagram of the orbital energy levels of the HO^- and ClO^- ions in nucleophilic attack on the nth substrate: AO—atomic orbital; E_n^*—energy level of the LUMO of the substrate. The remaining symbols have the same significance as in Fig. 1.

The relation between the proposed explanation of the α-effect and the description of an acid–base type interaction may be analysed within the framework of Edwards' equation[210]:

$$\lg (k/k_0) = \alpha E + \beta H,$$

where α characterises the ability of the substrate to accept electrons and form a covalent bond and β characterises the capacity of the substrate for coordination[4]. For α-nucleophiles, $\alpha > 0$ and $\beta \leq 0$, in contrast to ordinary nucleophiles, which do not exhibit an anomalous reactivity (for the latter, $\alpha = 0$ and $\beta \simeq 1$). The ratio α/β then becomes a measure of the factor controlling the reaction: if α/β is large, the reaction is controlled by boundary molecular orbitals; for low values of α/β, the course of the reaction is determined by the charges of the reactants, which should lead to a relation between the α-effect and the redox potentials. If the latter hypothesis is correct, it is to be expected that hydrazine should be oxidised more readily than ammonia, and its redox potential should be higher owing to the higher HUMO energy E^*_n. Experimental data confirm this: the redox potential of hydrazine is higher than that of ammonia[5].

The involvement of an anionic nucleophile in the reaction is accompanied by a decrease of the p,π- p,π electron orbital interaction, because one of these orbitals forms a σ bond. The interaction between p,π and σ orbitals is on the whole less intense than the p,π–p,π interaction; the latter entails an increase of the reactivity of the nucleophile. The foregoing considerations lead to the following conclusion: the positive α-effect is induced by the decrease in the course of the chemical reaction of the overlap integral of the orbitals containing lone-pair electrons; hence one may conclude that the manifestation of the α-effect is determined by the conformation of the α-nucleophile. On this basis, α-nucleophiles can be divided into two groups[5]:

(a) Nucleophiles of the type ROO^-, ClO^-, and RSS^-, which have high p,π orbital repulsion energies in the ground state. Such nucleophiles should exhibit an enhanced reactivity in reactions with both saturated and unsaturated substrates.

(b) The conformation of nucleophiles of the type NH_2NH_2, NH_2OH, and RSSR is such that the p,π–p,π (or sp^3–sp^3) repulsion in the ground state is reduced to a minimum; under these conditions, the orbital splitting is zero.

The conformations of the ground state and the rotational barriers in peroxides[211–213], disulphides[214], F_2O_2,[215] NH_2NH_2,[216,217] NF_2NF_2,[173,218,219] NH_2OH,[174] diarsines[220], and diphosphines[221] have been studied in detail and may be accounted for in terms of a simple rule, described above, concerning the relation between the α-effect and the overlap integral of orbitals with lone-pair electrons. Fig. 3 illustrates examples of these α-nucleophiles in the form of idealised Newman projections[5]. Their molecules should not exhibit the α-effect due to the repulsion of the p,π orbitals; the increase of nucleophilic reactivity noted in certain reactions should be attributed to other causes. For example, the anomalous reactivity of amidoximes in reactions with benzyl bromide is attributed to general intramolecular base catalysis[14].

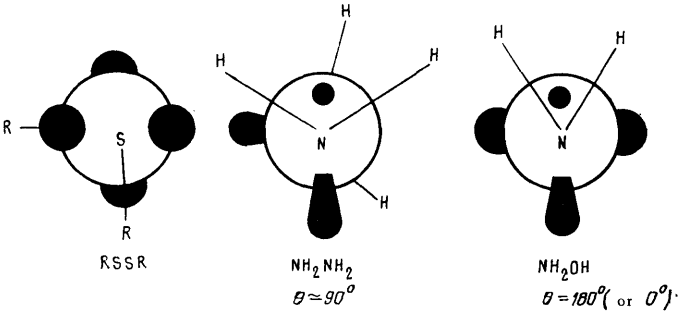


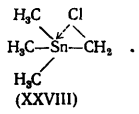
Figure 3. Idealised Newman projections for disulphides RSSR ($\theta = 90°$), hydrazine NH_2NH_2 ($\theta \simeq 90°$), and hydroxylamine NH_2OH ($\theta = 180°$ or $0°$). θ is the torsional angle.

However, one should note that the explanation of the α-effect based on the repulsion of the lone-pair electron orbitals suffers from a significant disadvantage. This is the assumption that the splitting of the energy level necessarily leads to an increase of the HUMO[190]. Quantum-chemical calculations and their thermodynamic analysis have shown, however, that the α-effect for NH_2NH_2 [190,222] and the ClO^- ion[190] cannot be explained solely by taking into account the orbital splitting.

6. Intramolecular Coordination

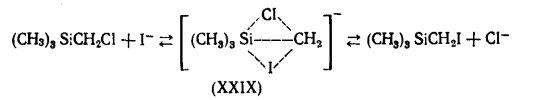
The anomalous behaviour of "mesoids" (α-carbofunctional compounds of Group IVB elements) is due to the effect of the intramolecular electronic interaction between M and Hal atoms; for example, the effect in chloromethyl(trimethyl)tin (XXVIII) is apparently due to the transfer of

the lone-pair electrons of the chlorine atom to the vacant *d* orbital of the Sn atom [223]:



(XXVIII)

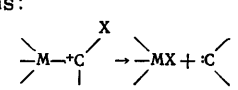
However, NQR data for "mesoids" with Ge, Si, and Sn atoms show that, together with the inductive effect of the substituents, there is intramolecular coordination between the atom of the Group IVB element and the halogen. The reactivity of $(CH_3)_3MCH_2Cl$ with respect to nucleophiles increases for different M in the sequence C < Si < Ge < Sn.[131] The latter shows that the site of nucleophilic attack is not only the carbon atom of the CH_2 group but also the M atom of the mesoid. For this reason, the relatively high reactivity of chloromethyl(trimethyl)silane has been explained[132] by the stabilisation of the transition state (XXIX) owing to the simultaneous interaction of the approaching halide ion with the carbon atom and the vacant 3*d* orbitals of the silicon atom:



(XXIX)

The outgoing Cl^- ion may interact with silicon and carbon atoms; a similar mechanism has been postulated for the reactions of chloromethyl(trimethyl)silane with SCN^- and $C_2H_5O^-$ ions.

The rearrangements involving the cleavage of the M–C bond and the migration of the substituent X from the carbon atom to the M atom constitute fairly convincing evidence for intramolecular coordination between the M and X atoms of mesoids:



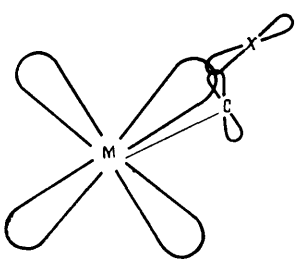


Figure 4. The formation of a three-centre bond of the "closed" type in "mesoids" (α-carbofunctional compounds of Group IVB elements).

The coordination interaction between the M and X atoms takes place with transfer of the σ electrons of the X atoms involved in the C–X bond to the vacant *d* orbitals of the M atom. This leads to the formation of a three-centre bond of the "closed" type[132] (Fig. 4) due to the overlapping of the p, σ orbitals of the X atom, the sp^3-hybridised orbitals of the carbon atom, and the vacant *d* orbitals of the M atom. The axes of these orbitals are directed to the interior of a non-equilateral triangle formed by the M, C, and X atoms. The occurrence of intramolecular coordination in mesoids has been questioned[224] in view of the very low coordination capacity of the M atom. The decreasing basicity of amino-derivatives of mesoids is pointed out in support of this view, while the Ge > Sn > Si series corresponds to the generally accepted electronegativity scale of the M atoms[224].

The ^{35}Cl NQR frequencies for alkyl chloromethyl ethers, which are appreciably lower than for alkyl chlorides, are attributed to the interaction between the lone-pair electrons of the oxygen atom and the σ electrons of the C–Cl bond in α-halogeno-ethers[225]. Voronkov[136,226] believes that the most likely explanation of the anomalous properties of the halogen atoms in α-halogeno-ethers is the direct interaction of the oxygen atom with the C–Cl bond and the formation of an intramolecular three-centre bond of the "closed" type (Fig. 5). This bond is formed between the O, C, and Cl atoms with participation of the sp^3-hybridised orbitals of the carbon atom, the p, σ orbitals of the chlorine atom, and the lone-pair electrons of the oxygen atom.

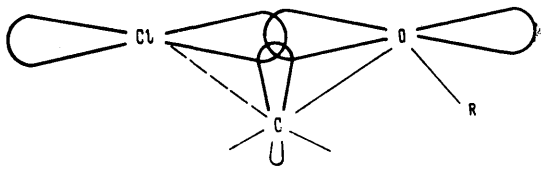


Figure 5. The formation of an intramolecular three-centre bond of the closed type in α-halogeno-ethers.

V. QUANTITATIVE ESTIMATE

Together with the qualitative description of the α-effect, it is of interest to consider the quantitative criteria for the assessment of this phenomenon. The increase of nucleophilic reactivity (i.e. the magnitude of the α-effect) has been estimated in terms of the ratio of the rate constants for reactions of α-nucleophiles and compounds which do not exhibit the α-effect (reference standards) when the basicities of both are the same; the α-effect varies significantly as a function of the type of nucleophiles used as the reference standards[79,164,166]. The latter were usually the HO^- ion, NH_3, glycine, and glycylglycine (Table 5). The α-effects in heteroaromatic compounds have been estimated as the ratios of the rate constants for the reactions of diazines and pyridine bases[32]. The ratios of the rate constants for the reactions of oximate and phenoxide (or alkoxide) ions of the same basicity were adopted as the α-effects in the reactions of 4-nitrophenyl acetate with oximate anions in water[9]. The α-effects in reactions with hydroxamic acids has been estimated as the ratios of the rate constants for the reactions of hydroxamic acids and phenoxide ions derived from phenols having the same p*K* values as the acids[189].

Table 5. Estimation of the α-effects in reactions of nucleophiles with various substrates.

Substrate	k (HOO^-)[a]/k·(HO^-)[b]	k (NH_2NH_2)[c]/k·(HO^-)	k (NH_2O^-)[d]/k·(HO^-)	k (ClO^-)[e]/k·(HO^-)	k (HOO^-)/k·($CF_3CH_2O^-$)[f]	k (NH_2NH_2)/k·(glycyl-glycine)[g]	k (NH_2NH_2)/k·(glycine amide)[h]	k (NH_2NH_2)/k·(NH_3)[i]
Benzonitrile	66 000[163]	—	—	—	—	—	—	—
4-Chlorobenzonitrile	22 000[163]	—	—	—	—	—	—	—
4-Methylbenzonitrile	19 000[163]	—	—	—	—	—	—	—
3-Bromobenzonitrile	35 000[163]	—	—	—	—	—	—	—
4-Cyanobenzoic acid	1 180[161]	—	—	—	—	—	—	—
Bromophenylacetic acid	12.7[161]	—	—	—	—	—	—	—
α-Bromo-4-toluic acid	13.1[161]	—	—	—	—	—	—	—
Bromoacetate	3.6[4]	23.2[4]	3.6[1]	—	—	—	—	8[4]
Ethyl acetate	10^{-4}[163]	—	—	—	—	—	—	—
Phenyl acetate	420[5]	$6.2\cdot10^{-3}$[5]	$9.2\cdot10^{-3}$[5]	—	80[230]	52[166]	—	4.65[232]
4-Methylphenyl acetate	—	—	—	—	—	—	—	2.77[232]
3-Nitrophenyl acetate	—	—	—	—	—	—	—	7.82[232]
4-Nitrophenyl acetate	386[5]	0.8[5]	0.2[5]	—	58[5]	44[166]	—	12.2[232]
2,4-Dinitrophenyl acetate	303[5]	5.5[5]	0.9[5]	—	41[5]	33[166]	—	—
1-Acetoxy-4-methoxypyridinium perchlorate	246[5]	0.8[5]	0.5[5]	—	51[5]	17[166]	—	—
Sarin	46.5[86]	—	10^{-3}[86]	—	0.3[86]	—	—	—
Diethyl 4-nitrophenyl phosphate	15.5[181]	—	—	—	—	—	—	—
Tetraethyl pyrophosphate	104[86]	—	1.2[86]	—	12.7[86]	—	—	—
4-Nitrophenyl phosphate	—	126[94]	40[94]	—	—	—	3.1[166]	—
2,4-Dinitrophenyl methyl phosphate	200[85]	—	1.0[85]	—	—	—	—	—
Benzyl bromide	34[14]	—	—	—	—	—	—	—
Methyl iodide	—	12.4[128]	—	—	—	—	5.0[166]	12.4[128]
Methyl tosylate	45.3[79]	—	—	—	62[79]	0.9[79]	—	—
Ethyl tosylate	—	3.0[4]	—	8.3[4]	—	—	—	—
4-Nitrophenyl sulphate	125[161]	—	—	—	—	—	6.0[166]	—
Malachite Green	10 810[79]	50.6[79]	7.3[79]	40.5[79]	—	28[164]	—	—
1-Fluoro-2,4-dinitrobenzene	45 000[79]	—	—	—	—	18.3[164]	19.4[166]	—
1-Iodo-2,4-dinitrobenzene	—	—	—	—	—	22.7[164]	21.3[166]	—
1-Chloro-2,4-dinitrobenzene	78 000[79]	3.5[227]	—	—	—	30.8[164]	35.6[166]	—
Picryl chloride	—	—	—	—	—	16.8[164]	23.2[166]	—
6-Acetoxyquinoline	—	—	—	—	—	38.0[27]	—	—
8-Acetoxyquinoline	—	—	—	—	—	25.2[27]	—	—
δ-Thiovalerolactone	—	3.1[120]	$6\cdot10^{-3}$[120]	—	—	—	—	—
Trifluoroethyl thioloacetate	—	3.2[228]	0.5[228]	—	—	—	—	—
Tris(acetylacetonato)silicate(IV) anion	47[129]	—	—	—	—	—	—	—
Methyl formate	—	—	—	—	—	250[231]	280[231]	—
Formaldehyde	166[130]	—	—	—	—	—	—	—
Acetaldehyde	13[130]	—	—	—	—	—	—	—
H_3O^+	10^{-4}[16]	10^{-8}[16]	10^{-10}[229]	10^{-8}[16]	—	—	—	—
trans-$Pt(Py)_2Cl_2$	—	—	—	—	—	—	—	6.3[127]
$RCOOH \rightleftharpoons RCOO^- + H^+$	0.61[155]	—	—	—	1.02[155]			

[a] $pK(HOO^-) = 11.60$. [b] $pK(HO^-) = 15.27$. [c] $pK(NH_2NH_2) = 8.11$. [d] $pK(NH_2O^-) = 6.20$. [e] $pK(ClO^-) = 7.10$. [f] $pK(CF_3CH_2O^-) = 12.36$. [g] pK(glycylglycine) = 8.25. [h] pK(glycine amide) = 8.10. [i] $pK(NH_3) = 9.21$.

One must note that the ratios $k(HOO^-)/k(HO^-)$ and $k(HOO^-)/k(NH_3)$ should be used with much caution as quantitative estimates of the α-effect, because the points on the Brønsted plots for HO^- and NH_3 very frequently lie below the straight line for primary amines and alkoxide ions; this finding apparently has nothing in common with the enhanced nucleophilic properties of the reactants due to the α-effect[71]. This probably explains the appreciable variation of the α-effect in reactions of aryl acetate esters (Table 5) and Malachite Green, for which Dixon and Bruice[79,164] estimated the α-effects as the ratios of the nucleophile/glycine, nucleophile/glycylglycine, and nucleophile/hydroxide ion rate constants.

The relative α-effects in the acylation reactions of hydrazine derivatives may be estimated as the ratios of the rate constants for the reactions of benzoylhydrazine and aniline with the same substrate[233]. Shevchenko[233] showed that the nucleophilic addition reactions (reactions with phenyl isocyanate) are the most sensitive to the α-effect and are followed, in this respect, by nucleophilic substitution at the carbonyl carbon atom (interaction with benzoyl chloride, ethyl chloroformate, phenyl chloroformate, and benzoic and acetic anhydrides). Substitution at an aromatic carbon atom (reactions of picryl chloride) exhibits an extremely insignificant α-effect. From our point of view, the ratio of the rate constants for the reactions of the given α-nucleophile and a primary arylamine of the same basicity must be regarded as a more correct estimate of the α-effect in hydrazine derivatives[104,234]. Table 6 presents quantitative estimates of the α-effect obtained using in certain cases the rate constants calculated by the Brønsted equations for the reactions of arylamines with phenyl chloroformate[234], phenyl isocyanate[234], phenyl thioisocyanate[104], benzoyl chloride[234], and picryl chloride[104]. In terms of the sensitivity to the α-effect, the substrates investigated can be arranged in the following sequence: phenyl isocyanate > benzoyl chloride > phenyl thioisocyanate > phenyl chloroformate > picryl chloride (Table 6). In reactions involving the hydrazides of phosphorus acids, those involving nucleophilic addition also exhibit the greatest α-effect; *N*-ethyl-substituted derivatives of these compounds show an α-effect smaller by a factor of 5–20 under the same conditions (Table 6).

Many workers have suggested a close relation between the α-effect and the β constant in the Brønsted equation[79,164,166]. A linear correlation has been noted between the magnitude of the α-effect and the β constant[166]. For hydrazine derivatives, correlations of this type are characterised by an appreciable scatter of the points, which can probably be accounted for by the fact that the basicity

constants of hydrazine derivatives and the rate constants for the reactions were measured in different media.

The linear correlation between $k(HOO^-)/k(HO^-)$ and the product $\alpha\beta$ of the coefficients of Edwards' equation for reactions employing ethyl acetate, 4-nitrophenyl acetate, 4-nitrophenyl methylphosphonate, 1-chloro-2,4-dinitrobenzene, α-bromo-4-toluic acid, and bromoacetic acid, which was noted by Behrman and coworkers [161], is promising for the quantitative estimation of the α-effect.

Table 6. Estimated α-effects in various reaction series involving hydrazine derivatives [104,123].

Hydrazine derivative	Phenyl chloroformate	Phenyl isocyanate	Picryl chloride	Hydrazine derivative	Phenyl chloroformate	Phenyl isothiocyanate	Picryl isocyanate
$RC_6H_4NHNH_2$	80	235	0	$(C_6H_5)_2PONHNH_2$	2772	331	32
$RC_6H_4N(C_2H_5)NH_2$	0	42	0	$(C_6H_5)_2PON(C_2H_5)NH_2$	565	173	37
C_6H_5N (Alk) NH_2	29	95	0	$(C_6H_5O)_2PONHNH_2$	1783	204	8
$RC_6H_4CONHNH_2$*	192	20 000	3	$(C_6H_5O)_2PON(C_2H_5)NH_2$	83	64	7
$RC_6H_4SO_2NHNH_2$	62	—	—	$(C_6H_5O)_2PSNHNH_2$	967	182	10
$AlkCONHNH_2$	—	3 600	—	$(C_6H_5O)_2PSN(C_2H_5)NH_2$	158	110	8

*In reactions with benzoyl chloride, the α-effect amounts to 7600.

Thus the foregoing findings show that a high reactivity (α-effect) is manifested by compounds with one or several lone-pair electrons at an atom adjoining the reaction centre. There are a wide variety of causes responsible for the α-effect, but none of them can fully explain its manifestations. In considering the α-effect in specific systems, one should probably take into account simultaneously a wide variety of factors which could explain this phenomenon.

It is noteworthy that an enormous amount of experimental data associated with the observation of the α-effect has accumulated largely as a result of the application of kinetic methods. Unfortunately there have been almost no studies on the nature of the α-effect by physical methods, and quantum-chemical procedures for calculations on reactions involving α-nucleophiles have also been inadequately used.

Despite the fact that the problem of the α-effect in organic compounds requires further systematic study and development, the relevant available information can already be used in analytical chemistry, in fine chemical organic syntheses on an industrial scale, and in the manufacture of physiologically active preparations and polymeric materials.

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