Translated from *Uspekhi Khimii*, 53, 566-582 (1984) U.D.C. 547.541

The Reactivity of Addends in the 1,3-Dipolar Cycloaddition Reaction

Ya.D.Samuilov and A.I.Konovalov

The influence of donor-acceptor interactions and localisation energies on the reactivity of addends in the 1,3-dipolar cycloaddition reaction is examined. It is shown that the interactions between the symmetric frontier orbitals and between the antisymmetric frontier orbitals are qualitatively different in $(4\pi + 2\pi)$-cycloaddition reactions. The effects arising as a result of the interaction of the symmetric frontier orbitals lead to an alteration of the position of the transition state on the potential energy surface for the reaction and increase the sensitivity of the 1,3-dipolar cycloaddition reactions to localisation effects.
The bibliography includes 113 references.

CONTENTS

I. Introduction 332
II. The influence of donor-acceptor interactions on the reactivity of addends in the 1,3-dipolar cycloaddition reaction 332
III. Qualitative differences between the effects arising as a result of the interaction of the antisymmetric and symmetric frontier orbitals in 1,3-dipolar cycloaddition reactions 335
IV. The influence of localisation effects on the reactivity of the addends in 1,3-dipolar cycloaddition 336

I. INTRODUCTION

The 1,3-dipolar cycloaddition reaction has been vigorously investigated in the last few decades. Interest in this field of study can be accounted for primarily by the fact that a wide variety of heterocyclic compounds, many of which have found extensive application, can be synthesised in a single stage under mild conditions with the aid of the 1,3-dipolar cycloaddition reaction. The theoretical ideas developed in the course of the investigation of this reaction not only promote the understanding of its mechanism and a number of fine details of intermolecular interactions but can also be used successfully in the study of other reactions. The enormous amount of experimental data on the 1,3-dipolar cycloaddition reaction, including the results of kinetic and preparative experiments, have now been surveyed in a series of reviews[1-9].

Both single-stage and two-stage mechanisms have been proposed for the 1,3-dipolar cycloaddition reaction. There is controversy in the literature concerning the type of mechanism which actually operates[10-13]. However, characteristic features of the 1,3-dipolar cycloaddition reactions such as the low sensitivity of the reaction rates to a change in the nature of the solvent[14-16], the weak influence of the substituents in the addends on the reactivity[17-20], the high negative activation entropies, low activation enthalpies, and large negative activation volumes[21], the exceptionally rigorous observation of the *cis*-principle,[22] and the kinetic isotope effects[23-25] agree to a large extent with a synchronous mechanism.

Quantum-chemical calculations of the potential energy surfaces for 1,3-dipolar cycloaddition reactions also indicate a synchronous mechanism of this process[26-34].

There have been reports that the reactions of diazomethanes with dipolarophiles having pronounced electron-accepting properties result in the formation of radical-ions[35-38] but so far it is impossible to solve unambiguously the problem of the role of these species in the reaction.

One of the most important tasks in the study of the 1,3-dipolar cycloaddition reaction is the discovery of factors which determine the reactivity of the addends. These data are essential for the prediction of the reactivity of systems, periselectivity, and stereoselectivity.

The present review is devoted to the consideration of the most important factors responsible for the reactivity of various 1,3-dipole–dipolarophile pairs. Analysis of kinetic data leads to the conclusion that a fairly complete description of the reactivities of such systems is possible only when account is taken simultaneously of the donor–acceptor interactions and the localisation effects. The existence of qualitative differences in the character of the interaction of the symmetric and antisymmetric frontier orbitals of the reactants in the 1,3-dipolar cycloaddition reaction has been established.

II. THE INFLUENCE OF DONOR–ACCEPTOR INTERACTIONS ON THE REACTIVITY OF THE ADDENDS IN THE 1,3-DIPOLAR CYCLOADDITION REACTION

It is nowadays believed that the reactivity of the addends in the 1,3-dipolar cycloaddition reaction depends mainly on the character of the intermolecular donor–acceptor interactions. Stabilisation energies are used for the comparative assessment of the donor–acceptor interactions[39-46]. They are calculated by methods of perturbation theory from the following formula:

$$\Delta E = 2\sum_{t}^{\text{occ}}\sum_{l}^{\text{unocc}} \frac{(C_t^{(l)}C_u^{(l)}\gamma_{tu} + C_{t'}^{(l)}C_{u'}^{(l)}\gamma_{t'u'})^2}{\varepsilon_{a_t} - \varepsilon_{b_l}} + 2\sum_{k}^{\text{occ}}\sum_{j}^{\text{unocc}} \frac{(C_t^{(j)}C_u^{(k)}\gamma_{tu} + C_{t'}^{(j)}C_{u'}^{(k)}\gamma_{t'u'})^2}{\varepsilon_{b_k} - \varepsilon_{a_j}}$$

where C_t are the coefficients of the atomic orbitals in the molecular orbital of the 1,3-dipole, C_u are the coefficients of the atomic orbitals in the molecular orbital of the dipolarophile, γ are interaction integrals, and ε are the energies of the molecular orbitals of the non-interacting systems. The summation is carried out over all possible combinations of the orbitals.

However, this formula is rarely used in specific calculations. In the interpretation of the experimental reactivity data in terms of stabilisation energies, it is usually sufficient to restrict the treatment to allowance for the interaction of the frontier orbitals and it is possible to neglect the differences between the coefficients of the atomic orbitals of the reaction centres[44,46,47]. As a result, the following simple expression is obtained for the stabilisation energy:

$$\Delta E = K\left(\frac{1}{\epsilon_{\text{HOO}}^{\text{1,3-dip}} - \epsilon_{\text{LUO}}^{\text{dip}}} + \frac{1}{\epsilon_{\text{HOO}}^{\text{dip}} - \epsilon_{\text{LUO}}^{\text{1,3-dip}}}\right).$$

Further simplifications in this formula may be associated with allowance for the relative disposition of the frontier orbitals of the addends. Sustmann[39] isolated three types of 1,3-dipolar cycloaddition reactions (Fig.1).

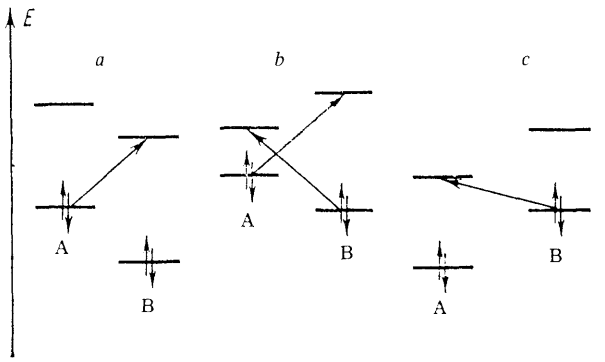


Figure 1. The relative disposition of the energy levels of the frontier orbitals of the addends in the 1,3-dipolar cycloaddition of the type where the 1,3-dipole and the dipolarophile are the donor and acceptor respectively (*a*), of the "neutral" type (*b*), and of the type where the 1,3-dipole and dipolarophile are the acceptor and donor respectively (*c*); A = 1,3-dipole; B = dipolarophile.

(1) The 1,3-dipole and the dipolarophile are the donor and acceptor respectively. In this case the interaction between the highest occupied orbital (HOO) of the 1,3-dipole and the lowest unoccupied orbital (LUO) of the dipolarophile is dominant.

(2) The "neutral" type. In this case the energy levels of the frontier orbitals of the 1,3-dipole are arranged symmetrically relative to the energy levels of the frontier orbitals of the dipolarophile.

(3) The 1,3-dipole and the dipolarophile are the acceptor and donor respectively. Reactions of this type obtain when the interaction between the lowest unoccupied orbital of the 1,3-dipole and the highest occupied orbital of the dipolarophile is dominant.

The usefulness of the above classification of the 1,3-dipolar cycloaddition reactions has been confirmed by numerous experimental data on the reactivity of the addends in the 1,3-dipolar cycloaddition reactions involving diazomethanes[48–52], nitrile imines[17], nitrile oxides[19,53,54], azides[55,56], etc. Fig.2 presents the dependence of the reactivities of a series of dipolarophiles in the 1,3-dipolar cycloaddition reactions with diazoacetic ester and dimethyl diazomalonate[50] on the ionisation potentials of alkenes. The figure shows that the type of reaction varies with the donor–acceptor characteristics of the dipolarophiles.

However, these and similar correlations may not be associated with a specific relative disposition of the energy levels of the frontier orbitals of the addends in the 1,3-dipolar cycloaddition reaction. Data on the reactivity of *C*-benzoyl-*N*-phenylnitrone in condensations with various dipolarophiles are of interest from this point of view. *C*-Benzoyl-*N*-phenylnitrone is a fairly powerful electron-accepting compound, its electron affinity is 1.0 eV, and its ionisation potential is 10.2 eV.[57] According to theoretical postulates, one might therefore expect that the type of reaction of this nitrone varies readily as the electron-donating character of the dipolarophile is altered.

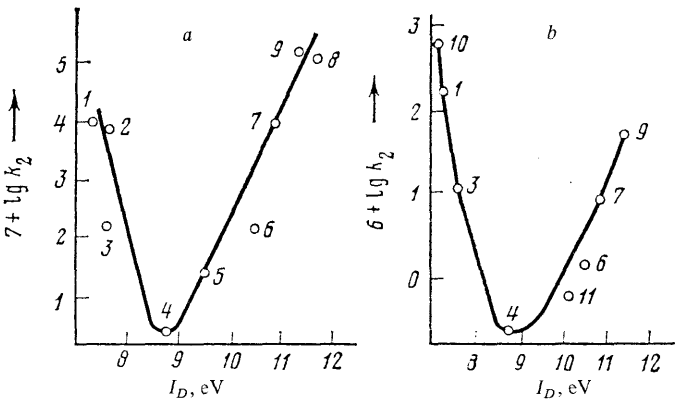


Figure 2. Dependence of the reactivities of diazoacetic ester (*a*) (toluene, 80 °C) and dimethyl diazomalonate (*b*) (mesitylene, 110 °C) in the 1,3-dipolar cycloaddition reaction on the ionisation potentials of the dipolarophiles[50]: *1*) pyrrolidinocyclohexene; *2*) 2-diethylamino-1-methylacetylene; *3*) 1,1-dimethyl-2-pyrrolidinoethylene; *4*) butyl vinyl ether; *5*) dec-1-ene; *6*) styrene; *7*) acrylonitrile; *8*) tetracyanoethylene; *9*) dimethyl acetylenedicarboxylate; *10*) pyrrolidinocyclopentene; *11*) methyl *trans*-crotonate.

In order to test this hypothesis, a kinetic study was made of the reactions of benzoylnitrone with a series of vinyl compounds (Table 1).[57,58] A symmetrical disposition of the energy levels of the frontier orbitals of the addends is attained in the reaction with acrylonitrile (Fig.3). However, the reduced reactivity of dipolarophiles with weaker electron-accepting properties than those of acrylonitrile shows that the entire reaction series belongs to the first type (where the 1,3-dipole and the dipolarophile are the electron donor and acceptor respectively).

Table 1. The reactivities of *C*-benzoyl-*N*-phenylnitrone in the 1,3-dipolar cycloaddition reactions with vinyl compounds (toluene, 20 °C).

Dipolarophile	$10^4 k_2$, litre mol^{-1} s^{-1}	lg *A*	E_A, kJ mol^{-1}	$-\Delta S^{\neq}$, J mol^{-1} K^{-1}
Acroleine	107.3	2.3	23	210
Acrylic acid	90.0	4.6	38	165
Methyl acrylate	44.6	5.4	44	150
Acrylonitrile	28.2	4.9	42	160
Allyl alcohol	14.9	3.9	39	179
Allyl methyl ether	1.4	8.3	69	94

In the reactions of *C*-benzoyl-*N*-phenylnitrone with styrene, the interaction between the lowest unoccupied orbital of the 1,3-dipole and the highest occupied orbital of the dipolarophile is much stronger than the interaction between the other two frontier orbitals (Fig.4). The reactions of styrenes with this nitrone should proceed in accordance with the third type (where the 1,3-dipole and the dipolarophile are the electron acceptor and donor respectively), but kinetic data have shown that the reactivity of arylethylenes determines the interaction between the highest occupied orbital of the nitrone and the lowest unoccupied orbital of the dipolarophile and the reactions proceed in accordance with the first type (with the 1,3-dipole and

dipolarophile as the electron donor and acceptor respectively),[58] this being confirmed by the correlation between the reactivities and the reciprocals of the differences between the ionisation potential of the nitrone and the electron affinities of the styrenes (Fig.5). Changes in the type of reaction are also not observed in the reactions of *C*-benzoyl-*N*-phenylnitrone with dipolarophiles having stronger electron-donating properties than styrenes, namely dipolarophiles such as aryl vinyl ethers[63] and aryl vinyl selenides[58]. Only in reactions with electron-donating dipolarophiles such as α-piperidinylstyrenes was it possible to observe a change in the type of reaction[63]. In this case a correlation is observed between the reactivities and the reciprocals of the differences between the ionisation potentials of the enamines and the electron affinity of *C*-benzoyl-*N*-phenylnitrone (Fig.6), which is evidence that the reaction proceeds in accordance with the third type (where the 1,3-dipole and the dipolarophile function as the electron acceptor and donor respectively).

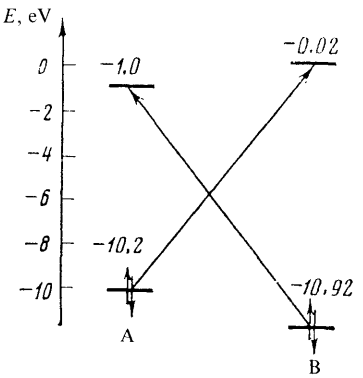


Figure 3. The relative disposition of the energy levels of the frontier orbitals of *C*-benzoyl-*N*-phenylnitrone (A) and acrylonitrile (B). The electron affinity and ionisation potential of acrylonitrile are based on the data of Houk and Munchausen[59].

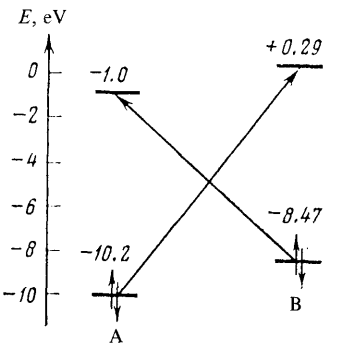


Figure 4. The relative disposition of the energy levels of the frontier orbitals of *C*-benzoyl-*N*-phenylnitrone (A) and styrene (B). The electron affinity and the ionisation potentials are based on the data of Hush and Pople[60] and Gurvich et al.[61] respectively.

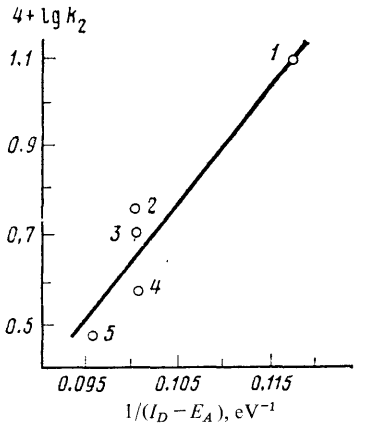


Figure 5. Dependence of the reactivity of *C*-benzoyl-*N*-phenylnitrone in the 1,3-dipolar cycloaddition reaction with styrenes of the type $R-C_6H_4-CH = CH_2$ [58] on the reciprocal of the difference between the ionisation potential of the 1,3-dipole and the electron affinity of the dipolarophile (toluene, 20 °C). The electron affinities of the styrenes were taken from Samuilov et al.[63]; R: *1*) *p*-NO_2; *2*) *p*-Br; *3*) *p*-Cl; *4*) H; *5*) *p*-CH_3O (r = 0.920).

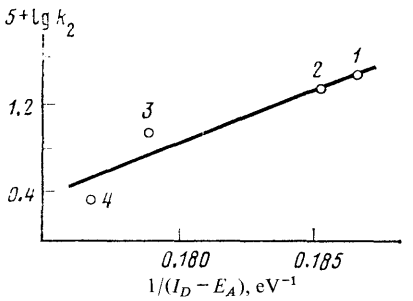


Figure 6. Dependence of the reactivity of *C*-benzoyl-*N*-phenylnitrone in the reaction with α-piperidinylstyrenes $RC_6H_4-CN(CH_2)_5 = CH_2$ on the reciprocal of the difference between the ionisation potential of the enamine and the electron affinity of the nitrone (toluene, 25 °C);[63] R: *1*) *p*-CH_3O; *2*) *p*-CH_3; *3*) H; *4*) *p*-Br.

The data presented indicate a clear preference for the interaction between the highest occupied orbital of the 1,3-dipole and the lowest unoccupied orbital of the dipolarophile compared with the interaction between the lowest unoccupied orbital of the 1,3-dipole and the highest occupied orbital of the dipolarophile. The above phenomenon is characteristic also of the Diels–Alder reaction[64–66]. It is of interest to note that even reactions of electron-accepting dienes such as tetrahalogeno-*o*-benzoquinones with styrenes proceed in accordance with the "neutral" diene synthesis[67], although there is no doubt that in such systems the interactions between the highest occupied orbitals of the styrenes and the lowest unoccupied orbitals of the quinones are much more intense than the interaction between the other two frontier orbitals.

It follows from the data presented that the character of the (4π + 2π)-cycloaddition reactions is probably determined by

the interaction between the highest occupied orbital of the four-electron π-system and the lowest unoccupied orbital of the two-electron π-system.

III. QUALITATIVE DIFFERENCES BETWEEN THE EFFECTS ARISING AS A RESULT OF THE INTERACTION OF ANTISYMMETRIC AND SYMMETRIC FRONTIER ORBITALS IN 1,3-DIPOLAR CYCLOADDITION REACTIONS

The above feature of the interaction of the frontier orbitals of the addends in the 1,3-dipolar cycloaddition reaction becomes understandable after more detailed analysis of the structure of the highest occupied orbital of the 1,3-dipole and the lowest unoccupied orbital of the dipolarophile (each of these orbitals is antisymmetric relative to the plane dividing the system in half) compared with the lowest unoccupied orbital of the 1,3-dipole or the highest occupied orbital of the dipolarophile (symmetric orbitals). The interactions of the frontier orbitals of these pairs lead to qualitatively different effects[68,69].

The formation of a chemical bond requires that the electron density be concentrated during the reaction in the space between the reaction centres. In the case of the synchronous mechanism, this condition is fulfilled for the antisymmetric frontier orbitals (Fig.7). The changes in the coordinates of the atomic nuclei of the interacting centres are in this case such that they promote the occurrence of the reaction. When symmetric frontier orbitals interact, a less favourable situation arises. Cross interactions lead to the localisation of the electron density in the inner part of the intermolecular space. Synchronous changes in the atomic coordinates of the reaction centres do not promote the occurrence of the reaction in this instance. Therefore, even in those cases where the energies of the symmetric frontier orbitals of the addends are fairly similar, nevertheless the antisymmetric orbitals are apparently responsible for the occurrence of the 1,3-dipolar cycloaddition reaction. From this standpoint, it becomes clear that the decisive influence, noted above, on the reactivity by the character of the interaction of the antisymmetric frontier orbitals rest on an entirely well-founded theoretical basis.

We may note an important consequence of the qualitative differences in the character of the interaction of the antisymmetric and symmetric frontier orbitals. When the interaction of the lowest unoccupied orbital of the 1,3-dipole and of the highest occupied orbital of the dipolarophile makes a significant contribution to the stabilisation energy, the contribution by the interaction between the other frontier orbitals can depend on the degree of localisation of the electrons in the reaction centres, which can lead to an alteration of the position of the transition state on the potential energy surface for the reaction and to its shift towards the adduct.

An approach to the interpretation of the reactivities of the addends in the 1,3-dipolar cycloaddition reaction in terms of localisation energies has been available[70,71] but has not come to be widely used. We believe that two approaches, based on the concepts of the stabilisation and localisation energies respectively, supplement one another. In estimating the stabilisation energies, no account is taken of the energy expenditure necessary for the localisation of electrons on the reaction centres. The two approaches describe different aspects of the process in which the transition state is established. An exact description of the reactivity in the 1,3-dipolar cycloaddition reaction is therefore possible only when both effects are taken into account.

In typical Diels–Alder reactions of the first type (where the diene and the dienophile are the electron donor and acceptor respectively) the symmetric frontier orbitals interact only slightly. The influence of the electron localisation effects on the reactivity is therefore insignificant in these reactions. The presence of heteroatoms more electronegative than carbon in the 1,3-dipoles leads to an appreciable enhancement of the electron-accepting properties of these systems[72]. An increased sensitivity to localisation effects should therefore be characteristic of the 1,3-dipolar cycloaddition reactions as a whole.

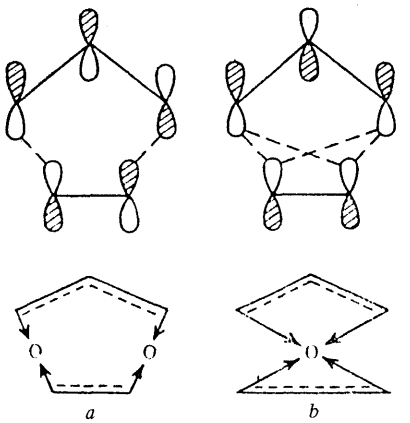


Figure 7. The frontier orbitals in the 1,3-dipolar cycloaddition reaction; *a*) the highest occupied orbital of the 1,3-dipole and the lowest unoccupied orbital of the dipolarophile (antisymmetric orbitals); *b*) the lowest unoccupied orbital of the 1,3-dipole and the highest occupied orbital of the dipolarophile (symmetric orbitals).

Correlations are possible in many instances between the stabilisation and localisation energies[73–75]. However, they are not general. Therefore, in interpreting reactivity, it is necessary to estimate each factor separately.

The localisation energies for the addends can be calculated by quantum-chemical methods. They can be estimated also with the aid of the enthalpies of the corresponding reactions, because the localisation energies and the enthalpies of reaction are linearly related[76].

The dependence of the position of the transition state on the potential energy surface on the character of the donor–acceptor properties of the addends has been discussed[71,77]. On the basis of simple geometrical constructions, the authors of the above studies concluded that an increase of the strength of the intermolecular donor–acceptor interactions leads to a shift of the transition state towards the adduct. We believe that this conclusion is insufficiently well-founded. In the general case donor–acceptor interactions leads to effects stabilising the transition state, which implies that the transition state can be established with a lower degree of formation of new bonds, which corresponds to a shift of the position of the transition state towards the addends.

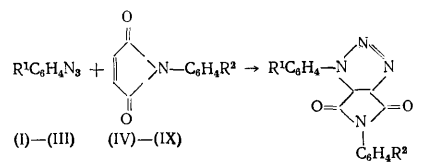
We may note in conclusion that the shift of the position of the transition state on the potential energy surface of the reaction towards the adduct is of the kind indicated in the above studies[71,77] and is associated with the characteristics of the symmetric frontier orbitals of the addends, which do not favour the reaction.

IV. THE INFLUENCE OF LOCALISATION EFFECTS ON THE REACTIVITY OF THE ADDENDS IN 1,3-DIPOLAR CYCLOADDITION

It is clear from the above analysis that the 1,3-dipolar cycloaddition reaction should be characterised by an increased sensitivity to changes in the localisation energies of the addends. When this factor is taken into account, certain anomalies observed for this reaction become understandable. Thus, it is known that 2,4,6-trimethylbenzonitrile oxide gives the "neutral" 1,3-dipolar cycloaddition reaction with styrenes[78]. The enhancement of the electron-accepting character of the dipolarophile should intensify the interaction between the antisymmetric frontier orbitals of the reactants and these reactions should proceed in accordance with the type where the 1,3-dipole and dipolarophile are the donor and acceptor respectively. However, kinetic study of the reactivity of *N*-arylmaleimides (dipolarophiles containing two carbonyl groups at the reaction centres, which ensures pronounced electron-accepting properties of these compounds) in the reaction with 2,4,6-trimethylbenzonitrile oxide[79] has shown that the influence of the substituents is manifested only slightly and the course of the reaction is inconsistent with the expected pattern. This result is not associated with the characteristic features of the transfer of electronic effects in the imides to the reaction centre via the bridging nitrogen atom; this has been confirmed in Diels–Alder reactions with imides, which proceed in accordance with the type where the diene and dienophile function as the donor and acceptor respectively[80,81], in which the accelerating influence of the electron-accepting substituents in the imides and the inhibiting effect of the electron-donating substituents is clearly manifested. Furthermore, the study of the polarographic reduction of *N*-arylmaleimides [82,83] also failed to reveal any characteristic features in the transfer of electronic effects to the multiple bond.

The unusual behaviour of *N*-arylmaleimides in the reaction with 2,4,6-trimethylbenzonitrile oxide is in all probability associated with the fact that the localisation energy increases with enhancement of the electron-accepting character of the substituents in these dipolarophiles[76]. In the reactions with imides, which proceed, according to the classification based on allowance for the donor–acceptor properties alone, in accordance with the type where the 1,3-dipole and the dipolarophile are the donor and acceptor respectively, there is therefore a possibility of cases where the substituents do not exert an appreciable influence on the reactivity or this influence diminishes with enhancement of the electron-accepting character of the dipolarophiles.

Kinetic data for the reactivity of aryl azides in the 1,3-dipolar cycloaddition reaction with *N*-arylmaleimides are of interest in this connection[84]:



R^1=*p*-CH_3O (I), H (II), *p*-NO_2 (III), R^2=*p*-$(CH_3)_2N$ (IV), *p*-CH_3O (V), *p*-CH_3 (VI), H (VII), *p*-Br (VIII), *p*-NO_2 (IX)

Fig. 8 illustrates the correlation between the reactivity of aryl azides in the reaction with arylmaleimides and the Hammett σ constants. It is seen that in the reactions of the azide (I) with the imides (IV)–(IX) there is a tendency towards an increase of the rate of reaction with enhancement of the electron-accepting character of the imides. In the reactions of the azide (II) with the imide (IV)–(IX), both electron-donating and electron-accepting substituents in the dipolarophile favour the reaction. In the case of the azide (III) the electron-donating substituents in the imides increase the rate of reaction, while the electron-accepting substituents reduce it.

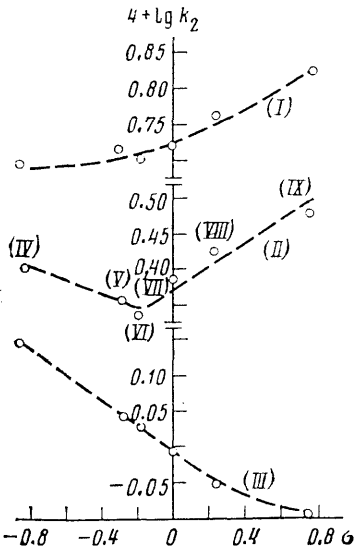


Figure 8. Dependence of the reactivities (lg *k*) of the aryl azides (I)–(III) in the reactions with the *N*-arylmaleimides (IV)–(IX) on the Hammett σ constants (chlorobenzene, 80 °C).[84]

The results obtained can be explained from the standpoint of the donor–acceptor properties assuming that an increase of the electron-donating character of the azide entails a change in the type of reaction from that where the 1,3-dipole and the dipolarophile are the acceptor and donor respectively to that where the roles are reversed. This conclusion conflicts with the reactivities of a series of azides in relation to individual imides: all the reactions indicated proceed in accordance with the type where the 1,3-dipole and the dipolarophile are the donor and acceptor respectively regardless of the electronic character of the substituents in the dipolarophile.

The observed changes in reactivity can be explained by assuming that the reactivity in the systems investigated is determined not only by the donor–acceptor properties but also by the localisation energies. If the role of these factors varies within the limits of one series, the non-linear correlations described above can arise. From this standpoint, the relative reactivity in reactions with the azide (I) (the azide having the most pronounced electron-donating properties among those investigated) is largely determined by the relative disposition of the energies of the frontier orbitals of the addends.

When the above azide is replaced by phenyl azide (II), which is a weaker electron donor, the role of the antisymmetric frontier orbitals diminishes, while that of the symmetric frontier orbitals increases, which leads to a displacement of the position of the transition state on the potential energy surface towards the adduct. The energy expended on the localisation processes increases and the stabilisation energy diminishes, which results in a decrease of the reactivity of the system. In reactions with imides

containing fairly strong electron-accepting groups in the aromatic ring, the reactivity is largely determined by stabilisation energies. If, on the other hand, arylmaleimides have electron-donating substituents, then the relative reactivity is determined by localisation energies. In the 1,3-dipolar cycloaddition reactions of the azide (III) with the imides (IV)–(XI) the interaction of the symmetric frontier orbitals is most intense for the series considered. The relative reactivity is controlled in this case solely by the localisation energies of the dipolarophiles, as shown by the correlation between the reactivities of the arylmaleimides in the reaction with the azide (III) and the enthalpies of the Diels–Alder reactions of compounds (IV)–(XI) with 1,3-diphenylisobenzofuran (Fig.9). The enthalpies of the reactions considered can be used to estimate the localisation energies of the imides. Fig.9 also presents the point corresponding to maleic anhydride, which is least reactive, although, compared with the imide[86], it is a stronger acceptor[85] and hence should have been more reactive.

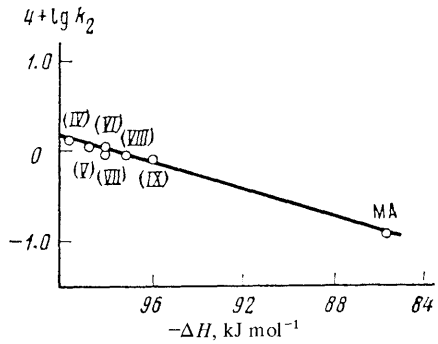


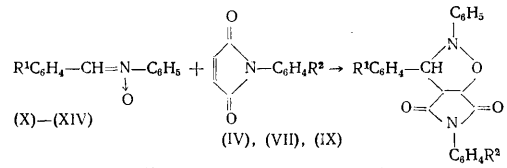
Figure 9. Dependence of the logarithms of the rate constants for the reactions of *p*-nitrophenyl azide (III) with the *N*-arylmaleimides (IV)–(IX) and maleic anhydride on the enthalpies of the reactions of these dipolarophiles with 1,3-diphenylisobenzofuran[84]; MA = maleic anhydride; $r = 0.995$.

The question arises whether the relative changes in reactivity in the above reactions with styrenes are also associated with localisation effects. The change in the electronic character of the substituents in the aromatic ring of styrenes hardly affects the localisation energies of these dipolarophiles, which has been demonstrated by quantum-chemical calculations[87] and has been confirmed by thermochemical experiments[88]. The relative reactivities of styrenes in the 1,3-dipolar cycloaddition reactions are therefore correlated with the stabilisation energies characterising the changes in the donor–acceptor properties.

All these data show that, within the limits of the same series, non-linear correlations can arise. The appearance of these correlations is associated with the change in the relative roles of the donor–acceptor interaction and the localisation effects. The non-linear correlations observed in the study of the 1,3-dipolar cycloaddition reaction have been analysed[89]. The author proposed a new modification of the Hammett equations based on the linearisation of correlations of this type. However, this approach is applicable only in those cases where the reactivity of the addends in several series is determined by at least two factors and the influence of one factor, responsible for the deviation from the Hammett equation, should be the same in all the series, while the influence of the second factor on the reactivity should be correlated with the Hammett σ constants. The applicability of this modification of the Hammett equation is extremely limited. In those cases where the relative roles of the factors determining the reactivity of the addends vary even within the limits of one series, the attempts to linearise the correlations are hardly useful.

The data on the reactivities of nitrones in 1,3-dipolar cycloaddition reactions also cannot be accounted for from the standpoint of the donor–acceptor properties alone. For example, it is known[90] that electron-accepting substituents in dipolarophiles increase their reactivity in reactions with nitrones. It would have been logical to expect that the electron-donating substituents in nitrones also accelerate the reactions. However, kinetic data have shown that both electron-donating and electron-accepting substituents reduce the reactivity in the reactions of *C*-aryl-*N*-phenylnitrones with ethyl crotonate[90]. The existence of such series is altogether incomprehensible from the standpoint of the method of stabilisation energies. In the reactions of *C*-phenyl-*N*-arylnitrones with ethyl crotonate[90], a decrease of the reactivity is observed following the introduction of electron-donating substituents. The hypothesis that these reactions proceed in accordance with the type where the 1,3-dipole and the dipolarophile are the acceptor and donor respectively is unlikely, because even in reactions of an electron-accepting nitrone, such as *C*-benzoyl-*N*-phenylnitrone, with styrenes, which have more pronounced electron-donating properties than ethyl crotonate, an accelerating effect of the electron-accepting substituents in the dipolarophile is observed. The joint kinetic and thermochemical study of the reactions of *C*,*N*-diarylnitrones with *N*-arylmaleimides made it possible to explain the existing phenomena[79,91,92].

Table 2 presents data on the reactivities of *C*-aryl-*N*-phenylnitrones in the 1,3-dipolar cycloaddition reaction with *N*-arylmaleimides and the enthalpies of reaction of these nitrones with *N*-phenylmaleimide:



R^1=*p*-NO_2 (X), *p*-Br (XI), H (XII), *p*-CH_3O (XIII), *p*-$(CH_3)_2$N (XIV)

Table 2. The reactivities of *C*-aryl-*N*-phenylnitrones in the 1,3-dipolar cycloaddition reactions with *N*-arylmaleimides and the enthalpies of the reactions of the nitrones with *N*-phenylmaleimide (toluene).[79,92]

Nitrone	*N*-(*p*-dimethylaminophenyl)-maleimide (IV)				$10^3 k_2$ for *N*-phenylmaleimide (VII), litre mol^{-1} s^{-1}	$10^{3*} k_2$ for *N*-(*p*-nitrophenyl)-maleimide (IX) litre mol^{-1} s^{-1}	$-\Delta H^{**}$, kJ mol^{-1}
	$10^{3*} k_2$, litre mol^{-1} s^{-1}	E_A, kJ mol^{-1}	lg *A*	$-\Delta S^{\neq}$, J mol^{-1} K^{-1}			
(X)	1.05	60	7.8	92	1.38	0.92	69.5
(XI)	1.68	54	6.8	109	2.15	1.70	74.9
(XII)	2.54	52	6.6	113	3.20	3.18	82.0
(XIII)	1.66	53	6.6	113	2.01	7.36	72.0
(XIV)	1.12	61	8.0	88	2.15	12.82	63.2

*At 20 °C.
**At 50 °C.

The accelerating effect of the electron-donating substituents in the 1,3-dipole and the inhibiting effect of the electron-accepting substituents, which is characteristic of reactions proceeding in accordance with the type where the

1,3-dipole and the dipolarophile are the donor and acceptor respectively, is manifested in the reactions of the nitrones (X)–(XIV) with the most electrophilic imide (IX). In this case the reactivity can be described satisfactorily in terms of the donor–acceptor properties of the addends alone, which is indicated by the correlation between the reactivities of the nitrones (X)–(XIV) and the reciprocals of the differences between the ionisation potentials of the 1,3-dipoles (I_D) and the electron affinities of the dipolarophiles (E_A) (the ionisation potentials of the nitrones have been determined by Samuilov et al.[93]):

$$\lg k = 25.05\ (I_D - E_A)^{-1} - 6.25\ (r = 0.960)$$

As the electron-donating character of the imides becomes more pronounced, the reactivity of the nitrones diminishes after the introduction of both electron-donating and electron-accepting substituents into the C-aromatic ring. The enthalpies of reaction vary analogously. The inclusion of the enthalpies of reaction, which are linearly related to the localisation energies of 1,3-dipoles, in the correlation equations together with the parameter describing the donor–acceptor interactions, makes it possible to describe the reactivity correctly in this instance. The correlations are based on the following parameters:

(1) for the imide (VII):

$$\lg k = 6.512\ (I_D - E_A)^{-1} - 0.019\ \Delta H - 5.016\ (r = 0.981)$$

(2) for the imide (IV):

$$\lg k = 0.662\ (I_D - E_A)^{-1} - 0.021\ \Delta H - 4.44\ (r = 0.938)$$

In terms of the sign of the coefficient of the reciprocal of the difference between the ionisation potential of the nitrone and the electron affinity of the imide, all the series investigated belong to reactions of the type where the 1,3-dipole and the dipolarophile are the donor and acceptor respectively. As the electron-donating character of the imide becomes more marked, i.e. as the interactions between the antisymmetric frontier orbitals are weakened and the interactions between the symmetric orbitals are intensified, the role of the localisation effects becomes successively more pronounced. Thus, in the series investigated, consecutive changes in the factors determining the reactivities of the compounds are observed.

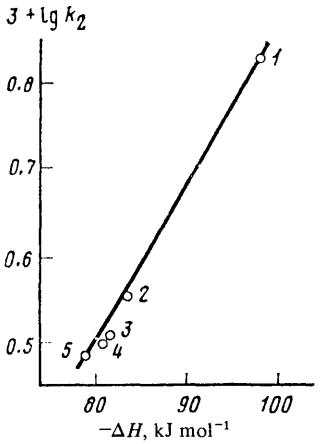


Figure 10. Dependence of the reactivities of *N*-aryl-*C*-phenylnitrones $C_6H_5CH = N(O)-C_6H_4R$ in the reactions with *N*-phenylmaleimide on the enthalpies of reaction (toluene, 20 °C);[92] R: *1*) *p*-NO_2; *2*) *p*-Cl; *3*) H; *4*) *p*-CH_3; *5*) *p*-CH_3O; $r = 0.990$.

Kinetic and thermochemical study of the reactivities of *C*-phenyl-*N*-arylnitrones with *N*-phenylmaleimide[92] showed (Fig.10) that the changes in reactivity in this case are parallel to the changes in the enthalpies of reaction, which can be regarded as an indication that the relative reactivities are in this case determined by localisation effects.

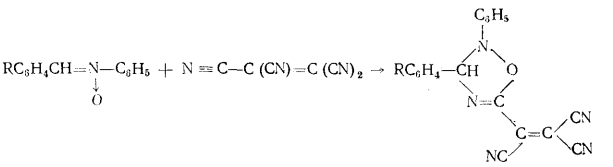
The inconsistency between the electron-donating properties of the nitrones and their reactivities in the 1,3-dipolar cycloaddition reaction with maleic anhydride has been demonstrated[63] (Table 3). In this case the reactivity also varies in parallel with the enthalpies of reaction. This permits the conclusion that in the reactions investigated the localisation effects play an important role, although the reactivity may partly depend also on polar effects[63].

Table 3. The activities of nitrones in the 1,3-dipolar cycloaddition reactions with maleic anhydride, the enthalpies of reaction with toluene, and the ionisation potentials of the nitrones[63].

Nitrone	$10^5 * k_2$, litre mol^{-1} s^{-1}	$-\Delta H_p^{**}$, kJ mol^{-1}	I_D, eV
C-Benzoyl-N-phenylnitrone	3460	84.5	10.2
C,N-Diphenylnitrone	61.1	65.7	7.3
N-Methyl-C-phenylnitrone	8.19	55.6	7.7

*At 20 °C.
**At 50 °C.

In reactions of nitrones with ethyl acrylate[90], *N*-arylmaleimides[79,92,99], and maleic anhydride[63], the influence of the localisation effects on the relative activities is manifested. In conformity with theoretical postulates, it might have been expected that the reactions of nitrones with dipolarophiles more electrophilic than those enumerated above would be controlled solely by the changes in the donor–acceptor properties. One of the most electrophilic dipolarophiles is tetracyanoethylene, whose electron affinity is 2.3 eV.[94] Indeed, the relative reactivities of *C*-aryl-*N*-phenylnitrones in their reactions with tetracyanoethylene are determined by the character of the changes in the electron-donating properties of the 1,3-dipoles (Fig.11).[93] However, the reactions investigated proceed via the carbon–nitrogen triple bond and not the carbon–carbon double bond[93]:



If these reactions were controlled solely by stabilisation energies, one would expect them to proceed via the carbon–carbon double bond, because the absolute coefficients of the atomic orbitals for the lowest unoccupied molecular orbitals of cyanoethylenes are highest for this bond[59] and in a typical Diels–Alder reaction of the type where the diene and the dienophile are the donor and acceptor respectively the reaction proceeds precisely via this bond[95,96]. A possible cause of the anomalous behaviour of nitrones is the greater strength of the $C_{sp^2}-C_{sp^2}$ π-bond compared with the $C_{sp}-N_{sp}$ π-bond. Thus the strength of the π-bond in ethylene estimated from the difference between the dissociation energies of ethylene and ethane is 314 kJ mol^{-1}, while the similar estimate of the bond strength in hydrocyanic acid is 293 kJ mol^{-1}.[97] The replacement of the hydrogen atoms

in ethylene by cyano-groups results in an additional increase of the strength of the carbon–carbon double bond[76]. The periselectivity of these reactions is apparently determined by the localisation energies.

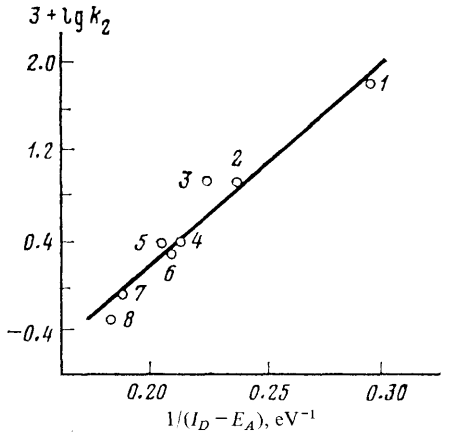


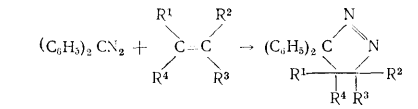
Figure 11. Dependence of the reactivities of *C*-aryl-*N*-phenylnitrones $RC_6H_4CH = N(O)-C_6H_5$ in their reactions with tetracyanoethylene on the reciprocal of the difference between the ionisation potential of the nitrone and the electron affinity of tetracyanoethylene (methylene chloride, 20 °C);[93] R: *1*) *p*-$(CH_3)_2N$; *2*) *p*-CH_3; *3*) H; *4*) *p*-Cl; *5*) *m*-Cl; *6*) *p*-Br; *7*) *m*-NO_2; *8*) *p*-NO_2; $r = 0.951$.

It is of interest to note that, whereas in the reactions of diazomethane[98] and diphenyldiazomethane[99] with tetracyanoethylene products resulting from addition to the carbon–carbon double bond are formed, diazoacetic ester[100] reacts with this dipolarophile via the carbon–nitrogen bond. In the first two instances, the attack is on the site corresponding to the most favourable interaction of the antisymmetric frontier orbitals of the addends, while in the third it is on the centres having the lowest localisation energies. It is remarkable that periselectivity changes in parallel with enhancement of the electron-accepting character of the 1,3-dipole, i.e. with increase of the contribution of the interaction of the symmetric orbitals to the stabilisation energy. The interaction via the carbon–nitrogen triple bond of tetracyanoethylene also takes place in reactions with nitrile sulphides, nitrile oxides[99], and certain other 1,3-dipoles.[101,102]

It was noted above that in a number of instances the stabilisation energy method has been used successfully to interpret the reactivities of dipolarophiles in reactions involving diazomethanes. However, the reactivity of diazo-compounds cannot always be described by taking into account only their donor–acceptor properties. For example, diazomethane is much more reactive in relation to 1,3-dipolar cycloaddition than diphenyldiazomethane[52]. Owing to the increase of the conjugation chain length on passing from diazomethane to diphenyldiazomethane, the energy levels of the frontier orbitals of the 1,3-dipoles approach one another, which can be seen from a comparison of the ultraviolet spectra ($\lambda_{max} = 395$ nm for diazomethane[103] and $\lambda_{max} = 527$ nm for diphenyldiazomethane[37]).

Polarographic data for the anodic oxidation of diazomethane and diphenyldiazomethane indicate an enhancement of the electron-donating character of the compound with increase of the conjugation chain length. Whereas the potential of the first reversible one-electron oxidation half-wave of diphenyldiazomethane at a rotating platinum disc electrode is 0.95 V relative to the saturated calomel electrode[104], for diazomethane the corresponding value is 1.7 V.[105] In view of these data, a higher reactivity of diphenyldiazomethane compared with diazomethane was to be expected. Apparently, the phenylation of diazomethane not only changes the donor–acceptor properties of the 1,3-dipoles but also increases the localisation energies. We may note that an increase of the localisation energies of dienes with increase of the degree of their phenylation had been convincingly demonstrated in earlier studies in relation to the diene synthesis reaction as a result of thermochemical studies of the reactions of butadiene and its phenylated derivative with tetracyanoethylene[106] and 4-phenyl-1,2,4-triazoline-3,5-dione[88]. Presumably a similar phenomenon obtains also in the case of diazomethane.

From the standpoint of the manifestation of qualitative differences between the effects of the interaction of the symmetric and antisymmetric frontier orbitals in 1,3-dipolar cycloaddition reactions, data on the reactivity of diphenyldiazomethane in relation to cyanoethylenes are of interest[107]:



(XV) (XVI)–(XX)

$R^1=R^2=R^3=H$, $R^4=CN$ (XVI); $R^1=R^3=H$, $R^2=R^4=CN$ (XVII); $R^1=R^4=H$, $R^2=R^3=CN$ (XVIII); $R^1=H$, $R^2=R^3=R^4=CN$ (XIX); $R^1=R^2=R^3=R^4=CN$ (XX)

The kinetic parameters of these reactions are presented in Table 4, which also includes the energies of the lowest unoccupied orbitals of the cyanoethylenes (XVI)–(XX) and the localisation energies calculated by the Hückel MO method[108]. It is seen from the data presented that the rate constants and activation energies for the reactions of compounds (XVI) to (XX) are inconsistent with their electron-accepting properties. The cyanoethylene (XVIII) shows the highest reactivity in the reaction with compound (XV), while the dipolarophile (XX), which is a much more powerful electron acceptor than compound (XVIII), reacts more slowly almost by a factor of 100. The variation in the reactivities of cyanoethylenes is also inconsistent with the localisation energy series.

Table 4. Kinetic parameters of the 1,3-dipolar cycloaddition reactions of the cyanoethylenes (XVI)–(XX) with diphenyldiazomethane in chlorobenzene[107] and the energies of the lowest unoccupied orbital (ε_{LUO}) and the localisation energies ($L_{1,2}$) of the dipolarophiles[108].

Cyanoethylene	k_2 litre mol^{-1} s^{-1}, 50 °C	lg *A*	E_A, kJ mol^{-1}	$-\Delta S^{\neq}$, J mol^{-1} K^{-1}	$-\varepsilon_{LUO}$, β	$L_{1,2}$, β
(XVI)	$4.5\cdot10^{-4}$	6.6	47	146	0.6891	2.462
(XVII)	$7.1\cdot10^{-4}$	6.1	51	130	0.6153	2.924
(XVIII)	10^{-2}	—	—	—	0.4826	2.888
(XIX)	13.8	5.2	21	155	0.4008	3.350
(XX)	0.38	4.8	28	159	0.2886	3.776

*At 5 °C.

Thus in the series investigated, the reactivity of the addends is not determined by the preferential influence of a particular factor and is in all probability determined by both factors. This is confirmed by the relation between the activation energies for the reactions of the cyanoethylenes (XVI)–(XX) with diphenyldiazomethane (XV) and the parameters (E_{LUO}, $L_{1,2}$) characterising the electron-accepting and

localisation properties of the dipolarophiles[107]:

$$E_A = -231.8\ (\varepsilon_{LUO} - 0.236\ L_{1,2}) - 250.2\ (r = 0.955).$$

(For a narrow range of compounds, in particular for cyanoethylenes, a linear correlation has been observed between the reciprocals of the differences between the ionisation potentials and the electron affinities and the ionisation potentials or electron affinities[59]. Direct correlations with I_D and E_A have therefore found extensive applications for the description of the reactivities in the series when allowance for the other reactant is unimportant[45].)

In terms of the sign of the constant preceding ε_{LUO}, the series investigated belongs to reactions of the type where the 1,3-dipole and the dipolarophile are the donor and acceptor respectively. The activation energy for the reaction of the cyanoethylene (XVIII) with diphenyldiazomethane calculated from the parameters of the equation is 20 kJ mol^{-1}. In the Diels–Alder reactions of cyanoethylenes with cyclopentadiene and 9,10-dimethylanthracene, which are typical electron-donating dienes, the reactivity of the dienophiles is consistent with their electron-accepting properties[109], while in the reactions of the same compounds with electron-accepting dienes such as substituted phenylcyclones[110] and tetracyclones[111] an appreciable influence of the localisation effects on the reactivities is manifested, although from the standpoint of the donor–acceptor properties these reactions are also of the type where the diene and the dienophile are the donor and acceptor respectively.

Table 5. The enthalpies of activation for the reactions ($\Delta H^{\neq}_{soln}$), the enthalpies of solution of tetracyanoethylene (ΔH^{TCE}_{reactn}) and *C,N*-diphenylnitrone (ΔH^{N}_{reactn}), and the enthalpies of transolvation of the reactants (ΔH^{react}_{solv}) and the transition state (ΔH^{ts}_{solv}) relative to chlorobenzene in the 1,3-dipolar cycloaddition reaction of *C,N*-diphenylnitrone with tetracyanoethylene[112].

Solvent	$\Delta H^{\neq}_{soln}$, kJ mol^{-1}	ΔH^{TCE}_{reactn}, kJ mol^{-1}*	ΔH^{N}_{reactn}, kJ mol^{-1}	ΔH^{react}_{solv}, kJ mol^{-1}	ΔH^{ts}_{solv}, kJ mol^{-1}
Chlorobenzene	56.9	23.1	22.6	0	0
Benzene	78.6	14.9	23.0	−7.8	13.9
Toluene	84.5	9.7	22.6	−13.4	14.2
o-Xylene	109.2	1.4	24.3	−20.0	32.3

*Konovalov et al.[113]

The usual influence of solvents on the reactivity, which can be explained in terms of the qualitative differences between the effects of the interaction of the symmetric and antisymmetric frontier orbitals of the addends, has been observed in the reaction of *C,N*-diphenylnitrone with tetracyanoethylene[112]. The kinetic and thermochemical data for this reaction are presented in Table 5. Evidently, the differences between the activation barriers in different reactions are not only caused by the differences between the solvation energies of the reactants but also depend significantly on the solvation energy of the transition state, the transolvation energy of the activated complex increasing with enhancement of the electron-donating character of the solvent. The observed trends in the transolvation of the transition state become understandable when account is taken of the possibility of a change in the position of the transition state on the potential energy surface.

Enhancement of the electron-donating properties of the solvent reduces the electron-accepting properties of tetracyanoethylene owing to complex formation processes. This entails a weakening of the interaction between the antisymmetric orbitals of the addends and an increase of the contribution to the stabilisation energy by the interaction of the symmetric orbitals. As a result of this, the transition state becomes more localised, i.e. it shifts along the reaction coordinate in the direction of the products. The energy consumed on the localisation increases the energy of the transition state, which parallels the enhancement of the electron-donating properties of the solvent and the diminution of the electron-accepting character of tetracyanoethylene. It is of interest to note that, in the Diels–Alder reaction of tetracyanoethylene with anthracene, the contribution to the stabilisation energy resulting from the interaction of the symmetric orbitals is low and an appreciable influence of the nature of the solvent on the energy of the transition state is not observed[113], which confirms the above point of view.

There is no doubt that the strong influence of solvents on the character of the reaction is possible only in the presence of specific solvation in the system. In those cases where the interaction of the addends with the solvent is weak the rates of 1,3-dipolar cycloaddition reactions change only slightly when the nature of the solvent is altered[14,90].

* * *

The above discussion shows that, for the interpretation of the reactivities of the addends in 1,3-dipolar cycloaddition reactions, it is necessary to take into account not only the donor–acceptor properties of the 1,3-dipoles and dipolarophiles but also the localisation energies of the corresponding reaction centres. While concentrating attention on these two factors, we naturally do not deny the existence of other electronic and steric effects. However, allowance for these factors alone makes it possible in a number of instances to describe the reactivity satisfactorily.

We believe that the qualitative differences in the character of the interaction of the symmetric and antisymmetric frontier orbitals are important. The understanding of the role of these interactions facilitates the prediction of the reactivities of addends in the $(4\pi + 2\pi)$-cycloaddition reaction and makes it possible to carry out a specific search for systems whose reactivity is determined mainly by a particular effect.

REFERENCES

1. R.Huisgen, Angew.Chem., 1963, **75**, 604.
2. R.Huisgen, Angew.Chem., 1963, **75**, 742.
3. R.Huisgen, R.Grashey, and J.Sauer, in "The Chemistry of Alkenes" [Edited by S.Patai, Wiley (Interscience), New York, 1964, pp.739–953] (Translated into Russian), Izd.Khimiya, Leningrad. Otd., Leningrad, 1969, p.444.
4. J.Bastide, J.Hamelin, F.Texier, and Y.Vo Quang, Bull.Soc.chim., France, 1973, Part II, 2555.
5. J.Bastide, J.Hamelin, F.Texier, and Y.Vo Quang, Bull.Soc.chim., France, 1973, Part II, 2871.
6. T.Kauffmann, Angew.Chem., 1974, **86**, 715.
7. R.Huisgen, Pure Appl.Chem., 1981, **53**, 171.
8. D.St.C.Black, R.F.Grozier, and V.C.Davis, Synthesis, 1975, 205.
9. N.G.Khusainova and A.N.Pudovik, Uspekhi Khim., 1978, **47**, 1507 [Russ.Chem.Rev., 1978(9)].
10. R.A.Firestone, J.Org.Chem., 1968, **33**, 2285.
11. R.Huisgen, J.Org.Chem., 1968, **33**, 2291.

12. R.Huisgen, J.Org.Chem., 1976, **41**, 403.
13. R.A.Firestone, Tetrahedron, 1977, **33**, 3009.
14. R.Huisgen, Pure Appl.Chem., 1980, **52**, 2283.
15. J.Geittner, R.Huisgen, and H.-U.Reissig, Heterocycles, 1979, Spec.Issue, **11**, 109.
16. V.A.Tartakovskii, A.A.Onishchenko, and S.S.Novikov, Izv.Akad.Nauk SSSR, Ser.Khim., 1967, 177.
17. A.Eckell, R.Huisgen, R.Sustmann, G.Wallillch, D.Grashey, and E.Spindler, Chem.Ber., 1967, **100**, 2192.
18. R.Huisgen and H.Gotthardt, Chem.Ber., 1968, **101**, 1059.
19. A.Dondoni and G.Barbaro, J.Chem.Soc., Perkin Trans.II, 1973, 1769.
20. A.Eckell, M.V.George, R.Huisgen, and A.S.Kende, Chem.Ber., 1977, **110**, 578.
21. N.S.Isaaks and E.Rannala, J.Chem.Soc., Perkin Trans.II, 1975, 1555.
22. W.Bihlmaier, J.Geittner, R.Huisgen, and H.-U.Reissig, Heterocycles, 1979, **10**, Spec.Issue, 147.
23. W.R.Doblier and D.S.Hong, Tetrahedron Letters, 1970, 4645.
24. W.F.Bayne and R.J.Snyder, Tetrahedron Letters, 1970, 2263.
25. B.M.Benjamin and C.J.Colline, J.Amer.Chem.Soc., 1973, **95**, 6145.
26. G.Leroy and M.Sana, Tetrahedron, 1975, **31**, 2091.
27. G.Leroy and M.Sana, Tetrahedron, 1976, **32**, 709.
28. D.Popinger, J.Amer.Chem.Soc., 1975, **97**, 7486.
29. D.Popinger, Austral.J.Chem., 1976, **29**, 465.
30. G.Leroy and M.Sana, Tetrahedron, 1976, **32**, 1379.
31. G.Leroy, M.T.Nguen, and M.Sana, Tetrahedron, 1976, **32**, 1529.
32. G.Leroy, M.T.Nguen, and M.Sana, Tetrahedron, 1978, **32**, 2459.
33. J.M.Lluch and J.Bertran, Tetrahedron, 1979, **35**, 2601.
34. P.Caramella, K.N.Houk, and L.M.Domelsmith, J.Amer.Chem.Soc., 1977, **99**, 4511.
35. T.Oshima, A.Yoshioka, and T.Nagai, Tetrahedron Letters, 1977, 1789.
36. T.Oshima and T.Nagai, Tetrahedron Letters, 1977, 3715.
37. T.Oshima, A.Yoshioka, and T.Nagai, J.Chem.Soc., Perkin Trans.II, 1978, 1283.
38. T.Oshima and T.Nagai, Bull.Chem.Soc.Japan, 1980, **53**, 726.
39. R.Sustmann, Tetrahedron Letters, 1971, 2717.
40. K.N.Houk, J.Sims, R.E.Duke, R.W.Strozier, and J.K.George, J.Amer.Chem.Soc., 1973, **95**, 7287.
41. R.Sustmann, Pure Appl.Chem., 1974, **40**, 569.
42. K.N.Houk, J.Sims, C.R.Watts, and L.J.Luskus, J.Amer.Chem.Soc., 1973, **95**, 7301.
43. K.N.Houk, Acc.Chem.Res., 1975, **8**, 361.
44. V.A.Tartakovskii and I.E.Chlenov, Zhur.Vses. Khim.Obshch.im.Mendeleeva, 1977, **22**, 252.
45. K.N.Houk, "Pericyclic Reactions", Pergamon Press, New York–San-Francisco–London, 1977, Vol.11, p.181.
46. L.A.Yanovskaya, "Sovremennye Teoreticheskie Osnovy Organicheskoi Khimii" (Modern Theoretical Principles of Organic Chemistry), Izd.Khimiya, Moscow, 1978, p.140.
47. H.Fujimoto and K.Fukui, in "Chemical Reactivity and Reaction Paths" (Edited by G.Klopman) (Translated into Russian), Izd.Mir, Moscow, 1977, p.30.
48. R.Sustmann, E.Wennig, and R.Huisgen, Tetrahedron Letters, 1977, 877.
49. J.Geittner, R.Huisgen, and R.Sustmann, Tetrahedron Letters, 1977, 881.
50. W.Bihlmaier, R.Huisgen, H.-U.Reissig, and S.Voss, Tetrahedron Letters, 1979, 2621.
51. R.Huisgen and J.Geittner, Heterocycles, 1978, **11**, Spec.Issue, 105.
52. L.Fisera, J.Geittner, R.Huisgen, and H.-U.Reissig, Heterocycles, 1978, **10**, Spec.Issue, 153.
53. K.Bast, M.Christl, R.Huisgen, and W.Mack, Chem. Ber., 1973, **106**, 3312.
54. A.Battaglia, S.M.Shaw, C.-S.Hine, and K.N.Houk, J.Org.Chem., 1979, **44**, 2800.
55. R.Sustmann, Tetrahedron Letters, 1974, 963.
56. M.K.Meilahn, B.Cox, and M.E.Munk, J.Org.Chem., 1975, **40**, 819.
57. S.E.Solov'eva, Candidate's Thesis in Chemical Sciences, Kazan State University, Kazan, 1980.
58. Ya.D.Samuilov, S.E.Solov'eva, A.I.Konovalov, and T.G.Mannafov, Zhur.Org.Khim., 1979, **15**, 279.
59. K.N.Houk and L.L.Munchausen, J.Amer.Chem.Soc., 1976, **98**, 937.
60. N.S.Hush and J.A.Pople, Trans.Faraday Soc., 1955, **51**, 600.
61. L.V.Gurvich, G.V.Karachevtsev, V.N.Kondrat'ev, Yu.A.Lebedev, V.A.Medvedev, V.K.Potapov, and Yu.S.Khodeev, "Energii Razryva Khimicheskikh Svyazei. Potentsialy Ionizatsii i Svrodstvo k Elektronu" (Chemical Bond Dissociation Energies, Ionisation Potentials, and Electron Affinities), Izd. Nauka, Moscow, 1974, p.236.
62. V.E.Gey, J.prakt.Chem., 1970, **312**, 823.
63. Ya.D.Samuilov, S.E.Solov'eva, and A.I.Konovalov, Zhur.Org.Khim., 1980, **16**, 1228.
64. Ya.D.Samuilov, A.I.Konovalov, and L.F.Uryadova, Zhur.Org.Khim., 1974, **10**, 1934.
65. A.I.Konovalov, Ya.D.Samuilov, L.F.Uryadova, and E.A.Berdnikov, Zhur.Org.Khim., 1976, **12**, 645.
66. N.D.Samuilov, L.F.Uryadova, and A.I.Konovalov, Zhur.Org.Khim., 1979, **15**, 977.
67. A.K.Konovalov, B.N.Solomonov, and O.Yu.Chertov, Zhur.Org.Khim., 1975, **11**, 110.
68. H.Fujimoto, S.Inagaki, and K.Fukui, J.Amer.Chem. Soc., 1976, **98**, 2670.
69. H.Fujimoto and T.Sugiyama, J.Amer.Chem.Soc., 1977, **99**, 15.
70. A.Streitwieser, "Molecular Orbital Theory for Organic Chemists" (Translated into Russian), Izd. Mir, Moscow, 1965, p.413.
71. K.-L.Mok and M.T.Nue, J.Chem.Soc., Perkin Trans.I, 1975, 1810.
72. P.Caramella, R.W.Gandour, J.A.Holl, C.G.Deville, and K.N.Houk, J.Amer.Chem.Soc., 1977, **99**, 385.
73. M.V.Bazilevskii, Zhur.Fiz.Khim., 1965, **39**, 1418 [Russ.J.Phys.Chem., 1965(6)].
74. M.V.Bazilevskii, Dokl.Akad.Nauk SSSR, 1967, **172**, 1105.
75. M.V.Bazilevskii, "Metod Molekulyarnykh Orbit i Reaktsionnaya Sposobnost' Organicheskikh Molekul" (The Molecular Orbital Method and the Reactivity of Organic Molecules), Izd.Khimiya, Moscow, 1969, p.286.
76. V.D.Kiselev, A.N.Ustyugov, I.P.Breus, and A.I.Konovalov, Dokl.Akad.Nauk SSSR, 1977, **234**, 1089.
77. A.Argile and M.-F.Ruasse, Tetrahedron Letters, 1980, **21**, 1327.
78. A.Battaglia and A.Dondoni, Ric.Sci., 1968, **38**, 201.
79. Ya.D.Samuilov, S.E.Solov'eva, and A.I.Konovalov, Zhur.Obshch.Khim., 1979, **49**, 637.

80. A.I.Konovalov, V.D.Kiselev, and Ya.D.Samuilov, Dokl.Akad.Nauk SSSR, 1968, **179**, 866.
81. Ya.D.Samuilov, L.F.Uryadova, B.N.Solomonov, and A.I.Konovalov, Zhur.Org.Khim., 1975, **11**, 1917.
82. Yu.N.Kargin, V.S.Kondranina, A.A.Kazakova, E.S.Batyeva, and Ya.D.Samuilov, Zhur.Obshch. Khim., 1976, **46**, 741.
83. V.Z.Kondranina, A.A.Kazakova, E.S.Batyeva, Ya.D.Samuilov, and Yu.M.Kargin, Zhur.Obshch. Khim., 1977, **47**, 1173.
84. N.D.Samuilov, A.I.Movchan, and A.I.Konovalov, Zhur.Obshch.Khim., 1980, **50**, 447.
85. G.P.Naletova, L.K.Stotskaya, and D.D.Monakova, Zhur.Obshch.Khim., 1981, **51**, 672.
86. S.R.Rafikov, G.P.Naletova, D.D.Monakova, and V.Sh.Shaikhrazieva, Zhur.Obshch.Khim., 1981, **51**, 693.
87. A.I.Konovalov, Ya.D.Samuilov, L.F.Slepova, and V.A.Breus, Zhur.Org.Khim., 1973, **9**, 2086.
88. I.P.Breus, Candidate's Thesis in Chemical Sciences, Kazan State University, Kazan, 1979.
89. E.Stefan, Tetrahedron, 1975, **31**, 1623.
90. R.Huisgen, H.Seidl, and I.Brüning, Chem.Ber., 1969, **102**, 1102.
91. Ya.D.Samuilov, S.E.Solov'eva, T.F.Girutskaya, and A.I.Konovalov, Zhur.Org.Khim., 1978, **14**, 1693.
92. Ya.D.Samuilov, R.L.Nurullina, S.E.Solov'eva, and A.I.Konovalov, Zhur.Obshch.Khim., 1978, **48**, 2586.
93. Ya.D.Samuilov, S.E.Solov'eva, and A.I.Konovalov, Zhur.Obshch.Khim., 1980, **50**, 138.
94. L.E.Lyons and L.D.Palmer, Austral.J.Chem., 1976, **29**, 1919.
95. R.Winkler, Uspekhi Khim., 1963, **32**, 1525 [Russ. Chem.Rev., 1963(12)].
96. N.S.Zefirov and D.I.Mikhankov, Uspekhi Khim., 1980, **49**, 637 [Russ.Chem.Rev., 1980(4)].
97. A.Gordon and R.Ford, "The Chemist's Companion" (Translated into Russian), Izd.Mir, Moscow, 1976, p.541.
98. J.Bastus and J.Gastells, Proc.Chem.Soc.(London), 1962, 216.
99. J.E.Franz, R.K.Howe, and K.H.Pearl, J.Org.Chem., 1976, **41**, 620.
100. R.Scribner, G.Sauser, and W.Prichard, J.Org. Chem., 1960, **25**, 1440.
101. H.C.Berk and J.E.Franz, J.Org.Chem., 1979, **44**, 2395.
102. E.N.Zil'berman, "Reaktsii Nitrilov" (The Reactions of Nitriles), Izd.Khimiya, Moscow, 1972, p.307.
103. J.W.Rabalais, J.M.McDonald, V.Scherr, and S.P.McClynn, Chem.Rev., 1971, **71**, 73.
104. W.Jugelt and F.Pragst, Angew.Chem., 1968, **80**, 280.
105. W.Jugelt and F.Pragst, Tetrahedron, 1968, **24**, 5123.
106. A.N.Ustyugov, Candidate's Thesis in Chemical Sciences, Kazan State University, Kazan, 1977.
107. Ya.D.Samuilov, A.I.Movchan, and A.I.Konovalov, Zhur.Org.Khim., 1981, **17**, 1205.
108. A.I.Konovalov, Doctoral Thesis in Chemical Sciences, Kazan State University, Kazan, 1973.
109. J.Sauer and R.Sustmann, Angew.Chem., 1980, **92**, 773.
110. Ya.D.Samuilov, S.V.Bukharov, and A.I.Konovalov, Zhur.Org.Khim., 1981, **17**, 121.
111. Ya.D.Samuilov, S.V.Bukharov, and A.I.Konovalov, Zhur.Obshch.Khim., 1981, **51**(6), 1368.
112. Ya.D.Samuilov, S.E.Solov'eva, and A.I.Konovalov, Dokl.Akad.Nauk SSSR, 1980, **255**, 606.
113. A.I.Konovalov, V.D.Kiselev, A.N.Ustyugov, and N.G.Gess, Zhur.Org.Khim., 1976, **12**, 2541.

Ul'yanov-Lenin Kazan State University