CORRELATION OF KINETIC DATA OF 1,3-DIPOLAR CYCLOADDITIONS OF C-BENZOYL-N-PHENYLNITRONES WITH THE HOMO ENERGIES OF FURAN DERIVATIVES

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Application of PMO treatment to 1,3-dipolar cycloaddition of C-benzoyl-N-phenylnitrone with furan derivatives is described. Ionisation potentials of 2-R-substituted furan derivatives (R = H, CH_3, C_2H_5, CH_2OH, CH_2OCOCH_3, C_6H_5, CHO) and 2,5-dimethylfurane representing experimental values of the HOMO energies have been determined from energies of the respective charge-transfer complexes with TCNE. Good correlation between *IP* and k_2 rate constants indicates that the reaction is controlled by the LUMO(nitrone)/HOMO(furan deriv.) interaction. Electron affinities of the furan derivatives were determined from *IP* and energies of π—π^* transitions using empirical equation $\Delta E(\pi—\pi^*) = IP — EA — 450{\cdot}58$ kJ mol^{-1}.

Our previous papers[1-3] dealt with reaction of C-benzoyl-N-phenylnitrone (*Va*) and 2-substituted furan derivatives (*Ia*–*g*, Table I). The 1,3-dipolar cycloaddition only proceeded with the furan derivatives having ionisation potential (IP) of lower value than 858·70 kJ mol^{-1}; *Ig* and methyl 2-furancarboxylate only gave decomposition products of reaction of nitrone *Va*. In this context it appeared interesting to follow the cycloaddition kinetics dealt with in the present paper along with correlation of the k_2 rate constants with the found energies of the frontier orbitals of the reactants. Literature gives cycloaddition kinetics of *Va* with ethyl crotonate[4], acrylic acid derivatives, and styrene derivatives[5].

RESULTS AND DISCUSSION

The cycloaddition kinetics of *Va* with the derivatives *Ib*–*d* and *II* (Scheme 1) was followed spectrophotometrically in absolute benzene at 52°C by measuring the nitrone *Va* absorbances at 316 nm (see Experimental). The said method could not be used for following the reaction kinetics with the derivatives *If*, *g*, because their absorption maxima overlap the followed wavelength, as well as that with *Ia* due

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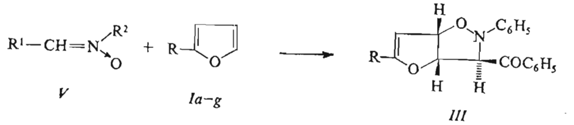
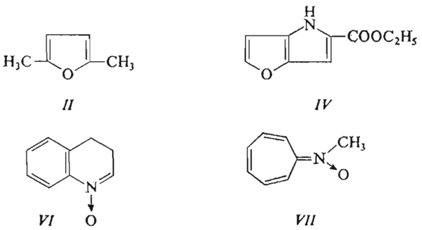
* Part CLV in the series Furan Derivatives; Part CLIV: *46*, 515 (1981).



a) $R^1 = C_6H_5CO$, $R^2 = C_6H_5$
b, $R^1 = H$, $R^2 =$ tert-C_4H_9
c, $R^1 = C_6H_5$, $R^2 = CH_3$
d, $R^1 = R^2 = C_6H_5$
e, $R^1 = R^2 = H$



Scheme 1
a—*g*, viz Tab. I.

to its low boiling point. The reaction was realized with a two hundred mol excess of the furan derivative, *i.e.* under the conditions of pseudomonomolecular reaction The high excess of furan derivatives is necessary to prevent formation of bis-adducts and side reactions of *Va* (ref.[1]). The second order rate constants k_2 were of 10^{-5} order of magnitude and were obtained from the quotient of $k_1\psi$ and concentration of the furan derivative at $\tau_{1/2}$ (Table I). The 1,3-dipolar cycloaddition of *Va* to 2-methylfuran is about 540 times slower than that to the derivatives having the same *IP* (the *IP* and *EA* energy values are given in kJ mol^{-1}) (styrene *IP* 813·36 and $k_2 = 3{\cdot}7 \,.\, 10^{-4}\, l\, mol^{-1} .\, s^{-1}$; phenylthioethylene $IP = 791{\cdot}17$ and $k_2 = 4{\cdot}36 \,.\, 10^{-4}\, l\, mol^{-1}\, s^{-1}$; 2-methylfuran $IP = 795{\cdot}99$ and $k_2 = 0{\cdot}8 \,.\, 10^{-6}\, l\, mol^{-1}\, s^{-1}$, the rate constants at 20°C), which corresponds to $\Delta\, \Delta G^{+} = 15{\cdot}49$ kJ mol^{-1}. The loss in the resonance energy of 2-methylfuran causes the difference $\Delta\, \Delta G^{+}$.

Early transition states of concerted cycloadditions enable application of the MO perturbation theory which is based on the orbital energies and atomic orbital coefficients of reactants[6]. Most applications of the perturbation theory to the 1,3-dipolar cycloaddition reactions are based on interaction between the frontier orbitals of 1,3--dipole and those of dipolarophile[7]. From perturbation theory it follows that the stabilization energy ΔE of the transition state being formed (which is given by the energy difference between the frontier orbitals) will be linearly proportional to the reaction rate. The hitherto knowledge about 1,3-dipolar cycloadditions of nitrones indicates enhanced reactivity of the dipolarophiles having electron-acceptor substi-

TABLE I

Energies (in kJ mol^{-1}) of CT Maxima of TCNE with Furan Donors and their Calculated *IP* and *EA*; Rate Constants of 1,3-Dipolar Cycloaddition

Compound	R	$\tilde{\nu}_{CT}$ [10^3 cm^{-1}]	λ_{CT} [nm]	E_{CT}	*IP*	$IP_{(lit)}$	π—π^*	*EA*	$k_2 . 10^5$ [$l\ mol^{-1}\ s^{-1}$]
Ia	H	23·4	427	279·80	850·02	856·77 (11) 867·39 (12)	569·25 (40)	—169·81	
Ib	CH_3	19·6	510	234·45	795·99	801·78 (38) 817·22 (12)	564·43	—219·01	4·25
Ic	C_2H_5	19·5	514	232·52	793·09	815·29 (12)	558·64	—216·12	4·77
Id	CH_2OH	21·1	474	252·78	819·14		550·92	—182·35	4·04
Ie	CH_2OCOCH_3	22·6	443	270·15	838·44		556·71	—168·84	
If	C_6H_5	16·5	607	196·82	755·47		436·10	—131·22	
Ig	CHO	25·8	388	308·74	879·93	888·61 (39) 916·59 (12)	449·61	—20·26	
II		17·5	573	208·40	768·97		550·92	—232·52	6·15
IIIa	H	17·9	559	214·19	775·73		484·35	—159·19	
IIIb	CH_3	17·7	565	212·26	773·80		484·35	—161·13	
IV		16·3	614	194·89	752·57				

tuents[4]. Leroy[8] used the *ab initio* method at the STO-3G base to calculate the activation energy $EA = 108{\cdot}85$ kJ mol^{-1} for the reaction of the parent hypothetical nitrone *Ve* with ethylene, the dominating frontier orbital interaction being HOMO(*Ve*) : : LUMO(ethylene), which means the *I.* type according to the Sustman classification[7]. In our paper[1] we stated that the cycloaddition of benzoylnitrone *Va* (in which the LUMO energy must be decreased dramatically by benzoyl group) to furan as a good donor is controlled by the frontier orbital interaction LUMO(*Va*)/HOMO(*Ia*). Therefore, for our purposes we could use the extensively simplified second order perturbation equation (*1*).

$$\Delta E = k\beta^2/(E_{\mathrm{HOMO(furan)}} - E_{\mathrm{LUMO(nitrone)}}) \qquad (1)$$

According to the Koopmans theorem[9] the ionisation potentials *IP* and the electron affinities *EA* represent, for practical purposes, the energies of the highest occupied (HOMO) and the lowest unoccupied molecular orbitals (LUMO), respectively, and the numerator in Eq. (*1*) can be considered constant for a series of very similar furan derivatives. As we used always the same nitrone *Va*, its *EA* value need not have been considered in the correlation. Hence, for the dominating interaction LUMO(*Va*)/HOMO(*I*) the reaction rate must be linear function of *IP* of the furane derivative *I*

$$\log k_2 \sim 1/IP\,. \qquad (2)$$

As calculations of the frontier orbital energies depend strongly on the method used, we determined the *IP* values experimentally. Literature[10] gives a number of methods for determination of *IP*, they are, however, usually quite expensive methods (PES), and, therefore, the *IP* values are only known for basic parent types of compounds. Out of the furan series used by us the *IP* values are known for furan (PES) (ref.[11]), 2-methylfuran and 2-furancarbaldehyde (photoionisation)[10]. For some furan derivatives the *IP* values were determined by mass spectrometry[12] (Table I). It is a drawback that the *IP* values were determined usually in gas phase, which makes the interpretation results of kinetic measurements in solutions difficult, the solvation contributions being neglected. Therefore, we calculated values of vertical *IP* of the furan derivatives from energies of charge-transfer (CT) $\pi-\pi$ molecular complexes by means of the Matsen equation[13].

$$h\nu_{\mathrm{CT}} = IP - c_1 + c_2/(IP - c_1)\,. \qquad (3)$$

The Eq. (*3*) gives satisfactory results for the CT complexes of the same acceptor and chemically similar donors, the *IP* values determined in this way differing from those obtained by the PES method by $\pm 9{\cdot}65 - 19{\cdot}30$ kJ mol^{-1}. The CT transition energies E_{CT} were determined by the method given in ref.[14,15], using tetracyanoethylene (TCNE) as the acceptor whose high *EA* value (173·67 kJ mol^{-1}) easily enables transition of one electron from the HOMO of furan to the LUMO of TCNE Solutions of the CT complexes were obtained by mixing $>10^{-3}$M-TCNE solutions in dichloromethane with $\sim 10^{-1}$M solutions of the furan derivatives. Isolation of the complexes in solid state failed. The values $c_1 = 588{\cdot}55$ kJ mol^{-1} and $c_2 = 52{\cdot}10$ kJ . . mol^{-1} in Eq. (*3*) were taken from ref.[16,17]. Also the constants $c_1 = 584{\cdot}69$ kJ mol^{-1} and $c_2 = 30{\cdot}87$ kJ mol^{-1} are known, but their application affects but slightly the *IP* values. The calculated *IP* values are given in Table I along with the literature data; there is a satisfactory agreement between the found *IP* values and those determined by the PES or photoionisation methods: *e.g.* for furan the *IP* value from CT complex is 850·02 kJ mol^{-1}, that from the PES method being 856·77 kJ mol^{-1}. Alkyl- and phenyl-substituted furans have much lower *IP* values than the parent compound, whereas the electron-acceptor substituent (*Ig*) increases the *IP* value only slightly as compared with furan. The given contributions of substituents correspond to those found by PES in alkene series. It is a well known fact that the *IP* values determined by mass spectrometry are usually slightly higher than those determined by the PES method. The values given in Table I agree with the said facts. The absorption maximum of the CT complex of furan and TCNE at 427 nm indicates that the complex is of $\pi-\pi$ type and not $n-\pi$ type. The absorption maximum of $n-\pi$ complex of tetrahydrofuran-TCNE lies at 318 nm[18,19], whereas $\pi-\pi$ complex benzene–TCNE absorbs at 387 nm (ref.[20]). Fig. 1 gives dependence of the CT transition energies on

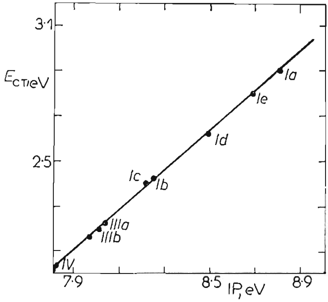


FIG. 1

Plot of Charge-Transfer Transition Energy (complex with TCNE) *vs* *IP* of the Furans

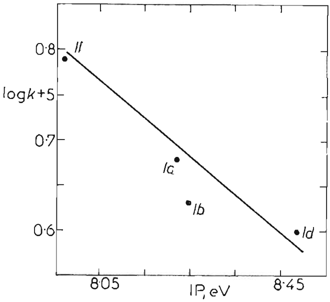


FIG. 2

Cycloaddition Rate Constants as a Function of *IP* of the Furans the calculated IP. The correlation obtained by the least squares method $h\nu_{CT} = 0{\cdot}89IP$ (furan) $-472{\cdot}77$ kJ mol^{-1} agrees well with that obtained[21] for substituted benzene derivatives $h\nu_{CT} = 0{\cdot}83IP$ (donor) $-426{\cdot}46$ kJ mol^{-1}. Literature gives for biphenyl the IP values 809·50 (ref.[14]) and 794·06 kJ mol^{-1} (ref.[22]); the value given in Table I for 2-phenylfuran (*If*) $IP = 755{\cdot}47$ kJ mol^{-1} proves the electron-donor character of furan nucleus attached to benzene ring. In this way we could indirectly confirm our previous results[23] where we obtained from pK_a constants the value $\sigma_p = -0{\cdot}1$ for 2-furyl substituent.

Furthermore, we determined the IP value of the monocycloadduct *IIIa* ($IP = 775{\cdot}73$ kJ mol^{-1}), which explains the contribution of the frontier orbitals to the higher yield of the bis-adducts as compared with mono-adducts in 1,3-dipolar cycloaddition of *Va* with small excess of furan[1]. The difference $\Delta IP = 70{\cdot}43$ kJ mol^{-1} between *IIIa* and *Ia* prefers secondary cycloaddition with the mono-cycloadduct *IIIa* to the primary cycloaddition with *Ia*. The IP values of *IIIa* agree well with those of 2,3-dihydrofuran derivatives or enol ethers[24]. In general the lowest IP value is observed with the derivative *IV* ($IP = 752{\cdot}57$ kJ mol^{-1}), *i.e.* lower than that of furan itself by 96·48 kJ mol^{-1}. Hence the derivative *IV* should be much more reactive in 1,3-dipolar cycloaddition with *Va*; in fact we found that *IV* reacts with *Va* already at room temperature to give quantitatively the mono-cycloadduct[25].

Fig. 2 gives the dependence between the measured rate constants k_2 and the calculated IP values of the furan derivatives. We obtained a relatively good correlation ($r = 0{\cdot}91$) in spite of considerable simplification of the second order perturbation equation (*1*). The obtained slope confirms that the 1,3-dipolar cycloadditions of benzoylnitrone *Va* with furan derivatives are controlled by the interaction LUMO-(nitrone)/HOMO(furan), *i.e.* opposite to the hitherto known cycloadditions of nitrones. It is difficult to decide whether the reaction is of the type *II* with the both interactions being significant or of the type *III* according to Sustmann[7], because we only followed the furan derivatives with electron-donor substituents. The relation obtained in Fig. 2 can also represent quite well the left part of an overall parabolic dependence (*U* curve with inclusion of electron-donor substituents) of the reaction rate *vs* IP characteristical for the type *II*. Investigation of kinetics of furans with electron-acceptor substituents was meaningless, because these compounds do not react with *Va* by 1,3-dipolar cycloaddition. Even in spite of that, we demonstrated that introduction of an electron-acceptor substituent into the nitrone molecule shifts the 1,3-dipole towards the type *II* or *III*. This case is the second one observed in 1,3-dipolar cycloadditions; the first case was observed recently by Huisgen in cycloadditions of diazocarbonyl compounds[26]. Therefore, it is surprising that cycloadditions of *Va* with styrene derivatives were classified[5] as the type *I*, although the IP values of the styrene derivatives resemble those of furans. It is obvious that the LUMO energies must be taken into account besides those of the HOMO. Out of furan derivatives the experimental EA value is only known for furan ($EA = -169{\cdot}81$ kJ mol^{-1}) which was determined by electron transmission spectroscopy[27,28]. Relative EA values of a series of similar derivatives can be approximated from the $\pi-\pi^*$ electronic transitions according to Eq. (*4*)

$$EA = IP - \pi-\pi^* - \Delta \qquad (4)$$

which was applied by Houk[29]. The value Δ = 450·58 kJ mol^{-1} was calculated from the known values of IP, EA and $\pi-\pi^*$ electronic transition of furan. The calculated value of Δ is close to Δ = 414·88 kJ mol^{-1} used for olefins[29]. The calculated values of EA of furan derivatives are given in Table I along with energy values of their $\pi-\pi^*$ electronic transitions obtained from UV spectra in hexane. The calculated value EA = −20·26 kJ mol^{-1} for 2-furancarbaldehyde (*Ig*) agrees with the expected greater effect of the electron-acceptor (as compared with electron-donor) substituents on the LUMO energy. The IP value of benzoylnitrone *Va*, which does not form CT complex with TCNE, is approximated in the following way: literature gives the value IP = 935·89 kJ mol^{-1} for the nitrone *Ve* ($R_1 = R_2 = H$) and the value of IP decrease 106·13 kJ mol^{-1} per one phenyl group introduced into the molecule of the nitrone *Ve* (ref.[29]). Hence the values IP = 723·63 and 829·76 kJ mol^{-1} are obtained for C,N-diphenylnitrone *Va* and N-phenylnitrone, respectively. From comparison of the IP values of monosubstituted ethylenes (electron-acceptor substituents with partial conjugation type —COR (ref.[29])) and from the well-known linear dependences of IP *vs* σ substituent constants[30] it is possible to derive an average contribution +19·30 kJ mol^{-1} per one benzoyl group. Hence for the benzoylnitrone *Va* we obtain the IP value 849·05 kJ mol^{-1}. This simple consideration is supported by very good linear dependence between the published[31,32] IP values of various nitrones and energies of their $\pi-\pi^*$ electronic transitions[33,34] (Fig. 3). For the

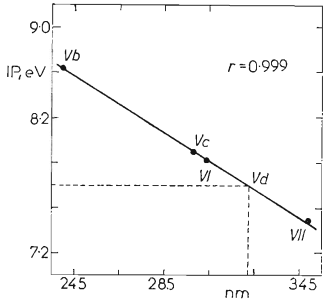


FIG. 3

Plot of IP of the Nitrones *vs* λ_{max} of the Nitrones nitrone *Vd*, for which we approximated the value 723·63 kJ mol^{-1}, the dependence gives the value 733·28 kJ mol^{-1}. Furthermore when comparing the *IP* values of diazomethane[35] (868·35 kJ mol^{-1}) and benzoyldiazomethane[36] (887·65 kJ mol^{-1}) we also get the difference of 19·30 kJ mol^{-1}. The equation given for calculation of *EA* with the value Δ = 354·09 kJ mol^{-1} (used for 1,3-dipoles[29]) gives for *Va* the value *EA* = = 84·90 kJ mol^{-1}. The authors[37] using the INDO method calculated for benzoylnitrone *Ve* the values $\varepsilon_{HOMO} = -995{\cdot}71$ kJ mol^{-1} and $\varepsilon_{LUMO} = 137{\cdot}97$ kJ mol^{-1}; for C,N-diphenylnitrone *Vd* the values $\varepsilon_{HOMO} = -926{\cdot}24$ kJ mol^{-1} and ε_{LUMO} = = 198·75 kJ mol^{-1}. Values of the HOMO energies obtained by the INDO method are usually greater by 144 – 193 kJ mol^{-1}, hence our approximated values seem quite acceptable. Using the determined values of the frontier orbitals we constructed the perturbation interaction diagram for 1,3-dipolar cycloadditions of benzoylnitrone *Va* with furan derivatives. For all the investigated furan derivatives exhibiting high values of the LUMO energies the dominant interaction is the LUMO(*Va*)/HOMO(*I*).

EXPERIMENTAL

The kinetic studies were carried out at the temperature 52 ± 0·1°C in absolute benzene up to 80% conversion. The concentration decrease of the starting substance *Va* was followed spectrophotometrically at the wavelength 316 nm. The absorbance was measured with the accuracy ±0·003, the temperature changed by 0·3°C during the experiment (about 50 h). The measurements were carried out with the automatic spectrophotometric system described in ref.[41]. In the time between the individual recordings the reaction mixture was protected from incident light by a spectrophotometric diaphragm. The first order rate constants $k_1\psi$ were calculated by the Guggenheim method[42] and divided by the furan concentration at half conversion to give the values k_2.

$$k_2(\text{cycloaddition}) = k_1\psi(\text{cycloaddition})/[I_{1/2}]\,.$$

Commercial TCNE was twice recrystallized from chlorobenzene and twice sublimed in vacuum. The UV-VIS spectra were measured in hexane using a Perkin–Elmer apparatus, those of the CT complexes were measured in dichloromethane (purified according to[43]) using a Specord spectrophotometer (Zeiss, Jena).

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