

Linear Free Energy Relationship for the Pressure Dependence of Rate Constants in Ene Reactions

(The Late) Boris El'yanov,^{a,†} Elena M. Gonikberg^{*,a} and Gérard Jenner^b

^a N. D. Zelinsky Institute of Organic Chemistry, USSR Academy of Sciences, Leninsky Prospect 47, 117913 GSP-1 Moscow, USSR

^b Laboratoire de Piézochimie Organique, EHICS, rattaché à l'Université Louis Pasteur, 1, rue Blaise Pascal, 67008 Strasbourg, France

The effect of pressure on rate constants of ene reactions involving (C...H...O), (C...H...C) and (O...H...O) hydrogen transfer is described by an equation of the linear free energy relationship type. Characteristic parameters of the equation are rather close to those obtained earlier for other types of nonpolar reactions with transition states involving the formation of new bonds. Activation volumes are calculated more precisely as compared with the commonly accepted methods, thus allowing us to find a strong linear dependence of activation volume on the logarithm of the rate constant in the reaction series of alk-1-enes with dimethyl mesoxalate. The reaction volume profile is described, its estimated parameters being in line with the experimental ones according to the accepted mechanism. The calculations point to processes which are not fully concerted.

It was found earlier¹⁻³ that the influence of pressure on rate and equilibrium constants of many chemical reactions can be described by an equation of the linear free energy relationship type (LFER), e.g. eqn. (1). Here φ is the pressure function

$$\lg k_P = \lg k_0 - \frac{\Delta V_0^\ddagger}{T} \times \varphi \quad (1)$$

which is common for each type of related reactions, and ΔV_0^\ddagger is the activation volume at atmospheric pressure.[¶]

A number of quantitative relationships and dependencies were obtained as thermodynamic consequences of eqn. (1). The following linear dependencies [eqns. (2-4)] from the same

$$\Delta S_P^\ddagger = \Delta S_0^\ddagger - m\varphi \quad (2)$$

$$\Delta H_P^\ddagger = \Delta H_0^\ddagger + n\varphi \quad (3)$$

$$\rho_P = \rho_0 + r\varphi \quad (4)$$

parameter φ are very useful. Here ΔS^\ddagger and ΔH^\ddagger are entropy and enthalpy of activation, respectively, and ρ is the reaction constant in the Hammett equation or in another similar LFER; the other functions

$$\begin{aligned} m &= R \ln 10 \cdot \Delta V_0^\ddagger K_0 \\ n &= R \ln 10 \cdot \Delta V_0^\ddagger (1 - TK_0) \\ \text{with } K_0 &= (1/\Delta V_0^\ddagger)(\partial \Delta V_0^\ddagger / \partial T) \\ r &= (-1/T)(\partial \Delta V_0^\ddagger / \partial \sigma) \end{aligned}$$

with σ the substituent constant in the Hammett equation.

Owing to these relationships, the problem of the description of the pressure effect on kinetic and thermodynamic parameters can be simplified by dividing it into two separate independent problems. On one side it is necessary to determine the

dependence of $\varphi(P)$ for each class of reactions and, on the other hand to find the parameters characteristic of an individual reaction (ΔV_0^\ddagger) or corresponding class of related reactions (K_0, r) at atmospheric pressure.

The analytical expression of the dependence φ on P was derived by assuming the Tait equation holds valid for the compressibility of liquids [eqn. (5)].

$$\varphi = [(1 + \alpha)P - (\alpha/\beta)(1 + \beta P) \ln(1 + \beta P)] / R \ln 10 \quad (5)$$

Parameters α and β are characteristic of each type of related reaction. It was found that α can be assumed identical for all reaction types and equal to 0.170. The value of β can be evaluated by means of statistical treatment of all the data available for the dependence of rate constants of the related reactions series on pressure. In this case $\lg k_{0i}$, ΔV_{0i}^\ddagger and β are considered as adjustable parameters ($i = 1, 2 \dots n$; n is the number of reactions in the series). Their most probable values correspond to the minimum of the function M given by eqn. (6), which is found for eqns. (1) and (2) with some

$$M = \sum_{i=1}^n (g_i - 2.5) \ln S_{0i} \quad (6)$$

fixed values of β [g_i is the number of experimental points for the i th reaction, S_{0i} is the standard deviation calculated by the least-squares method (LSM)].

Owing to the availability of numerous kinetic data, the value of β can be calculated with high accuracy, thus making it possible to describe quantitatively the pressure effect on kinetic parameters of this reaction type. Eqns. (1)-(5) can also be applied to precision calculations of ΔV_0^\ddagger , K_0 and $(\partial \Delta V_0^\ddagger / \partial \sigma)$ values, as well as to $\lg k_0$, ΔS_0^\ddagger , ΔH_0^\ddagger and ρ_0 .[§]

A systematic study of reactions of various types was carried out from the above point of view in order to (i) describe the quantitative regularities of the pressure effect on kinetic and thermodynamic parameters, (ii) study the influence of various factors on β , ΔV_0^\ddagger , K_0 and $(\partial \Delta V_0^\ddagger / \partial \sigma)$ -values, and (iii) apply these parameters to the study of the transition state (TS) and the reaction mechanism.

In the present paper such a study was carried out with ene reactions of the following general type. These reactions are

[†] Deceased August 1990.

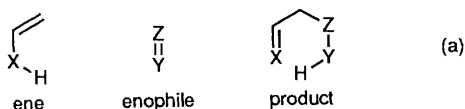
[¶] For the sake of simplicity we consider here kinetic parameters, though all the regularities are valid for the thermodynamic ones as well.

[§] This method of calculation of the latter four functions is of special interest if the reaction proceeds at a measurable rate only at high pressure.

Table 1 Activation volumes of ene reactions^a

	$-\Delta V_{\ddagger}^{\ddagger}/\text{cm}^3 \text{ mol}^{-1}$			Applicability of eqn. (1)			$-\Delta V_{25}^{\ddagger}$ ^d ($\text{cm}^3 \text{ mol}^{-1}$)	$\Delta V^{\ddagger}/\Delta \bar{V}$ at 25 °C	
	This work eqn. (1)	Graphic method ^c	Eqn. (9)	r_{corr}	Test of linearity	Abbe test		This work	See <i>c</i>
I. Reactions with DMMX, 110 °C									
(1) Hex-1-ene	48.2 ± 0.7	39	43.5	0.9995	+	+	35.3	1.31	1.05
(2) 3-Methylpent-1-ene	44.3 ± 2.3	36	35.4	0.9907	+	+	32.5	1.23	0.99
(3) 2,4,4-Trimethylpent-1-ene 2-Ethylbut-1-ene	49.8 ± 0.5	44	45.9	0.9998	+	+	36.4	1.18	1.04
(4) (<i>E</i>)-product	57.5 ± 1.9 ^b	48	64.0	0.9979	+	+	42.1	1.34	1.12
(5) (<i>Z</i>)-product 2,3-Dimethylbut-1-ene	53.2 ± 2.5 ^b	45	59.8	0.9955	+	+	39.0	1.24	1.05
(6) Tertiary abstraction	45.7 ± 2.2	45	52.8	0.9952	+	+	33.5	1.05	1.03
(7) Primary abstraction	47.0 ± 2.8	46	58.2	0.9930	−	+	34.4	1.07	1.05
II. Other reactions									
(8) β-Pinene + DEMX, 52.2 °C	34.5 ± 0.8	35	27.6	0.9989	+	+	30.9	1.05	1.06
(9) β-Pinene + DMAD, 96.4 °C	55.8 ± 3.5	52	65.9	0.9902	+	+	42.7	1.21	1.12
(10) Acetone + DEMX, 97 °C	45.1 ± 1.5	30	37.2	0.9984	+	+	34.4	1.00	0.88

^a DMXX = dimethyl mesoxalate, DEMX = diethyl mesoxalate, DMAD = dimethyl acetylenedicarboxylate. Original kinetic data: reactions 1–7, see ref. 6; reactions 8–9 see ref. 9; reaction 10, see ref. 7; standard deviation is given as an error. ^b The *k*-value at *P* = 1315 bar was excluded from the calculation. ^c Values from original papers. ^d Calculated from ΔV_{\ddagger} by method from ref. 2.



regarded as pericyclic, concerted, one-step processes.⁴ However, there is also evidence for a two-step course in some ene reactions. In some cases a radical-chain mechanism has been proposed.⁵

One of us^{6–9} has studied the pressure effect on the rate of ene reactions with (X...H...Y) hydrogen abstraction of various types. It was shown that in the studied (C...H...O), (C...H...C) and (O...H...O) hydrogen-transfer reactions, a $|\Delta V^{\ddagger}| \geq |\Delta \bar{V}|$ relationship occurs (ΔV^{\ddagger} and $\Delta \bar{V}$ are activation and reaction volumes at atmospheric pressure, both values being negative). This was interpreted as evidence in favour of (i) a concerted mechanism, even with angular hydrogen abstraction.⁶ For the processes of the (C...H...N) type in the reactions of cyclic alkenes, allylbenzene and α -methylstyrene with diethyl azodicarboxylate $|\Delta V^{\ddagger}|$ is considerably lower than $|\Delta \bar{V}|$, this being apparently indicative of two-step mechanisms. We have used the results of kinetic measurements in the 0–133 MPa pressure range obtained in these works for our calculations.

Results and Discussion

1. Linear Free Energy Relationship [eqn. (1)].—The reactions listed in Table 1 were taken as a basis for the statistical calculation of the value of β . It has been shown earlier that each reaction proceeds *via* a cyclic TS. Testing of the results (see below) which had been obtained after the initial treatment of the experimental data for all ten reactions casted doubt on the applicability of eqns. (1) and (5) to the data on the reaction given in entry 7, and for this reason the latter were excluded from the basis calculations. Repeated treatment of the data gave a value of β equal to $(4.51 \pm 1.12) \times 10^{-2} \text{ MPa}^{-1}$.

The straight lines fitted by LSM in line with eqn. (1) are given in Fig. 1. For each parallel reaction (entries 4 and 5) the last point falls outside the straight lines, obviously due to the error in determining the total reaction rate. These points were excluded from the LSM calculations. In all cases, except

entry (7) no systematic deviations from the constructed straight lines were observed within the limits of experimental accuracy.

For a more objective verification of the applicability of eqn. (1) we have used, as in our previous papers, a number of statistical tests.^{2,10,11} As seen from Table 1, the linearity test casts doubt on the applicability of eqn. (1) only in the case of the reaction shown in entry 7. In addition to the special tests given in Table 1 for each reaction, two general goodness-of-fit tests of eqn. (1) which covered the totality of the data on the discussed reactions, *i.e.* error randomness and Abbe tests, were applied. The value of ω_{expt} (see ref. 11) is equal to 0.5, thereby confirming the validity of the error randomness test. For the general Abbe test $\gamma = 0.7976$, while a minimal admissible value γ_{min} is equal to 0.7512, the test being also fulfilled.¹⁰ Therefore, eqn. (1) and (5) with $\alpha = 0.170$ and $\beta = 4.51 \times 10^{-2} \text{ MPa}^{-1}$ are applicable to ene reactions of the discussed types.

The values of $-\Delta V_{\ddagger}^{\ddagger}$ calculated by eqn. (1) in some cases considerably exceed those evaluated graphically by Evans and Polanyi from eqn. (7). However, we cannot ascribe this to the

$$(\partial \ln k / \partial P)_{P=0} = -\Delta V_{\ddagger}^{\ddagger} / RT \quad (7)$$

errors resulting from our method of calculation since statistical tests do not detect systematic deviations of experimental points from the $\lg k = f(\varphi)$ straight lines, except in entry 7.

Some additional information on this question can be obtained from the graphs in Fig. 1. It is easy to show¹² that eqn. (8) strictly follows from eqn. (7) for any function $\varphi^*(P)$, such as $(\partial \varphi^* / \partial P)_{P=0} = 1/R \ln 10$.

$$(\partial \lg k / \partial \varphi^*)_{P=0} = -\Delta V_{\ddagger}^{\ddagger} / T \quad (8)$$

The dependence $\lg k = f(\varphi^*)$ should not necessarily be linear. If, as suspected, some values of $(-\Delta V_{\ddagger}^{\ddagger})$ calculated by us are overestimated, then dependencies of $\lg k$ *vs.* φ should be reflected by curves which are convex downward near $P = 0$. However, such a deviation exceeding random scattering of experimental points cannot be visualized on the graphs of Fig. 1.

The use of quadratic eqn. (9) is the most popular method for calculating $\Delta V_{\ddagger}^{\ddagger}$ at present.¹³ Here $a = -\Delta V_{\ddagger}^{\ddagger} / RT$. LSM

$$\ln k_p = \ln k_0 + aP + bP^2 \quad (9)$$

estimates calculated by this method are also presented in Table 1.

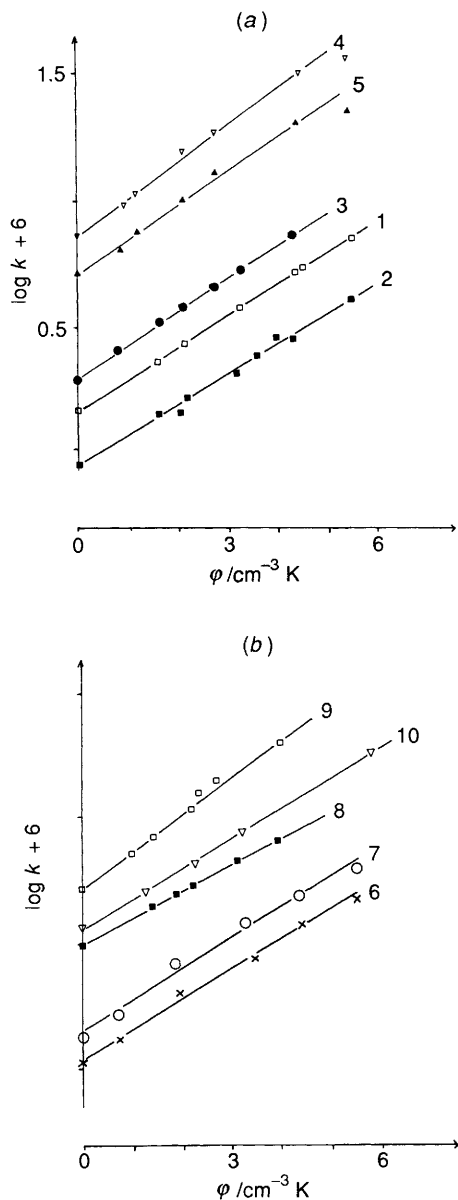


Fig. 1 Dependence of $\lg k$ on ϕ [eqn. (1)], enumeration of reactions from Table 1

The obtained values in some cases greatly differ from those calculated by the other two methods without any tendency to approach either of them. It will be shown below that only the calculation with the help of eqn. (1) permitted us to lower the level of noise resulting from random errors and to find out the regular character of activation volume change in the series of reactions.

The value of $\beta = 4.51 \times 10^{-2} \text{ MPa}^{-1}$ for ene reactions turned out to be rather close to the values calculated previously from kinetic data for other nonpolar reactions, such as Diels-Alder² ($\beta = 4.94 \times 10^{-2} \text{ MPa}^{-1}$), radical abstraction of hydrogen atom¹⁴ ($\beta = 4.15 \times 10^{-2} \text{ MPa}^{-1}$) and [3,3]-sigmatropic shift¹⁵ reactions ($\beta = 7.12 \times 10^{-2} \text{ MPa}^{-1}$) characterized by the formation of new bonds in the TS. All these values are very close to the average value of β , $3.91 \times 10^{-2} \text{ MPa}^{-1}$, calculated earlier³ from nonkinetic data on reaction volumes in various processes and proposed as the first approximation for calculations by eqns. (1) and (5). This impressive similarity of the β -values in reactions of various types is an additional valid argument in favour of the accepted assumption of the β equality for the related reactions of the same type. This confirms our findings on the LFER, eqn. (1)

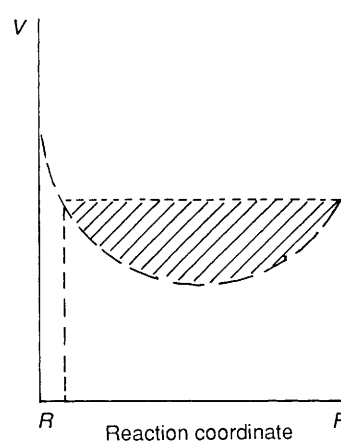
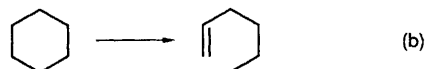


Fig. 2 Volume profile of ene reactions. R: reagents, P: product, TS_c is in the hatched region

being obviously quite a precise dependence,³ at least, for the great number of reaction types.

To conclude we should note that for certain types of reactions the value of β can considerably differ from the above values. Therefore, for the homolytic bond scission, the value of β was found¹⁶ to be an order of magnitude less ($0.36 \times 10^{-2} \text{ MPa}^{-1}$), but for Menshutkin reactions with polar TS it turned out considerably greater ($19.4 \times 10^{-2} \text{ MPa}^{-1}$ for reactions in acetone).¹² From the β -values, $B = [-(\partial \Delta V^\ddagger / \partial P) / \Delta V^\ddagger]_{P=0} = \alpha \beta$ can be calculated with good accuracy. These values, being characteristic of each class of related reactions, can therefore be considered both empirically and theoretically and used as a tool in mechanistic studies.^{12,16}

2. Activation Volume and Reaction Mechanism.—(a) *Reaction volume profile.* For general reasons it is expected that either concerted or two-step ene reactions would have the volume profile given in Fig. 2. The region in the vicinity of the minimum in the profile corresponds to a cyclic structure that ought to be more compact than either the reagents R or the product P, both of which have an open structure. Therefore a cyclic transition state (TS_c) is likely to exist in the hatched region. The maximum depth $(\bar{V}_p - \bar{V}_c)_{\text{max}}$ can be roughly estimated as follows. The



reaction cyclohexane \longrightarrow hex-1-ene may be used as an approximate analogue of the process $\text{TS}_c \longrightarrow \text{P}$. For this reaction,¹⁷ $\bar{\Delta V}_{2.5} = 17.2 \text{ cm}^3 \text{ mol}^{-1}$. This value may be divided into two parts¹⁸ as shown in eqn. (10) where ΔV_w is the change

$$\bar{\Delta V} = \Delta V_w + \bar{\Delta V}_{\text{free}} \quad (10)$$

of van der Waals (proper) volume and $\bar{\Delta V}_{\text{free}}$ is the free volume change including the change of void ($\Delta \bar{V}_v$), zero vibration at $T = 0$ ($\Delta \bar{V}_{zv}$) and expansion volumes ($\Delta \bar{V}_E$) (see ref. 19). In accord with the estimates¹⁷ of Asano and le Noble, $\bar{\Delta V}_w = 4.5 \text{ cm}^3 \text{ mol}^{-1}$ for reaction (b). As for the step $\text{TS}_c \longrightarrow \text{P}$ in the ene reaction (a), we can probably safely assume that $\Delta V_w = 0$ taking into account the minor volume of hydrogen ($\sim 4.4 \text{ cm}^3$) and the compensation of contributions resulting from the completion of X-H scission and formation of the Y-H bond. Hence $(\bar{V}_p - \bar{V}_c) \sim 13 \text{ cm}^3 \text{ mol}^{-1}$, this value being the free volume change only. According to the estimates made in ref. 17, $\bar{\Delta V}_E \sim \bar{\Delta V}_{zv} + \bar{\Delta V}_v \sim 6 \text{ cm}^3 \text{ mol}^{-1}$ for reaction (b). We can suggest that these estimates are also approximately true for the respective maximum values of the step $\text{TS}_c \longrightarrow \text{P}$ in reaction (a).

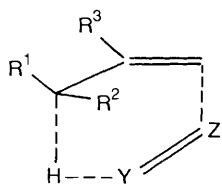


Fig. 3 Probable structure of TS_C . $R^1, R^2, R^3 = H$ or a substituent

Taking into consideration the estimates of $(\bar{V}_p - \bar{V}_C)$, it is possible to make another useful approximation. Hence, according to Jenner,^{6,9} $\Delta\bar{V}_{25}^\ddagger \sim (-31 \pm 4) \text{ cm}^3 \text{ mol}^{-1}$. Therefore for the ene reactions proceeding via the cyclic TS, $31 \leq (-\Delta V_{25}^\ddagger) \leq 44$ and $1 \leq \Delta V^\ddagger/\Delta\bar{V} \leq 1.4$. The correctness of these estimates is confirmed by the data in Table 1.

(b) *The dependence of activation volume on reaction rate.* It was shown in ref. 6 that with a pressure increase in the 0–370 MPa range, the *E*:*Z* ratio (isomers of the adduct in the reaction of 2-ethylbut-1-ene with DMMX at 110 °C) increases regularly from 1.33 to 1.74. This is reflected in the activation-volume values, $(\Delta V_{110}^\ddagger)_E - (\Delta V_{110}^\ddagger)_Z = -4 \text{ cm}^3 \text{ mol}^{-1}$ (entries 4 and 5 in Table 1). However, the opposite effect could have been expected, *i.e.* the portion of the (*Z*)-isomer being formed via a more sterically hindered TS should have increased with the increase in pressure.¹¹

In our search for the explanation of this result, we turned to the radical abstraction of hydrogen atoms. For this type of reaction in the absence of considerable polar and steric effects, Zhulin *et al.*²⁰ have found that more rapid reactions are to a greater extent accelerated by pressure. The pressure effect on the *E*:*Z* ratio discussed here falls into this regularity. In this case a linear relationship [eqn. (10)] has been observed. Here $a < 0$,

$$\Delta V^\ddagger = \Delta V_{st}^\ddagger + a \cdot \lg(k'/k'_{st}) \quad (11)$$

the 'st' index is assigned to the standard reaction, and $k' = k/s$ where s is the number of equivalent hydrogen atoms at the site of their abstraction by the radical. This number is generally considered to be equal to their total number at the corresponding carbon atom.

We decided to test the validity of eqn. (11) to ene reactions. Which of the hydrogen atoms will be equivalent in this case? As seen from an examination of the probable structure of the cyclic TS (Fig. 3), only one hydrogen atom is preferentially attacked. The breaking C–H bond should be oriented most closely to the p-orbital appearing in its place and oriented parallel to the neighbouring p-orbital. Therefore, s is equal to 1 in the case where substituents R^3 and CHR^1R^2 differ, and $s = 2$ if they are identical. It was found that the reaction series of alk-1-enes with DMMX at 110 °C fitted eqn. (11) with the correlation coefficient $r_{corr} = 0.9939$ (Fig. 4a). Therefore, this equation uniformly describes the influence of pressure both on the reaction rate and on its stereoselectivity. The parameters of eqn. (11) were evaluated by LSM and gave the values of $\Delta V_{st}^\ddagger = (-44.9 \pm 0.3) \text{ cm}^3 \text{ mol}^{-1}$ (the reaction with $k = 1 \times 10^{-6} \text{ mol}^{-1} \text{ s}^{-1}$ at 110 °C was conventionally taken as a standard) and $a = (-22.2 \pm 1.1) \text{ cm}^3 \text{ mol}^{-1}$. It should be noted that such a large absolute value for a is observed here for the first time. In the previously studied hydrogen abstraction processes, $|a| \leq 5$.

The three above methods for calculation of ΔV^\ddagger are compared with each other in Fig. 4. It can be seen that only application of eqn. (1) allowed us to find a clearly regular dependence [eqn. (11)]. It should be noted that this dependence was established for the results of ΔV^\ddagger obtained from direct kinetic measurements, in contrast to the former $(\Delta V^\ddagger - \Delta V_{st}^\ddagger)$ values calculated from more accurate measurements of the product ratio in competitive processes.²¹ These results, as well

as those obtained previously,^{11,14,22} indicate the advantage of LFER for precision calculations of ΔV^\ddagger , thus permitting the revelation of even minor effects.

From the above estimates of the limitations of ΔV_{25}^\ddagger we can state that $42 \leq (-\Delta V_{110}^\ddagger) \leq 60$ at 110 °C. Extreme values of the rate constants which are to limit the applicability of eqn. (11), namely $0.73 \leq 10^6 k' \leq 4.8$ at 110 °C (k' expressed in $\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$), correspond to this range. Evidently rather considerable changes of activation volume are to occur over a very narrow range of reaction-rate-constant changes. It would be extremely interesting to check the correctness of these limitations of eqn. (11) over a broader range of rate-constant changes.

For a qualitative explanation of the $a < 0$ relationship in eqn. (11) a hypothesis concerning the dominating role of quantum chemical tunnelling of hydrogen atoms has recently been proposed.²⁰ Tunnelling takes place at the reaction co-ordinate which is less than that of the TS. Therefore, for the earlier TS, when it is on the descending branch of the volume profile, a considerable contribution of tunnelling to the reaction rate should lead to a decrease in the (observed) value of $(-\Delta V_{obs}^\ddagger)$. Supposing that the decrease in activation energy lowers the tunnelling correction and thus increases the value of $(-\Delta V_{obs}^\ddagger)$, one arrives at the desired explanation for the phenomenon of stronger acceleration of faster reactions by pressure. However, this explanation is rather doubtful when applied to ene reactions. Achmatovicz and Szymoniak⁴ have estimated that TS in these reactions are late, *i.e.* that they occur on the ascending branch of the volume profile though, in this case, according to Zhulin's model, the value of a should be positive.

The obtained result for ene reactions can be rationalized if one suggests that the change of ΔV^\ddagger can be accounted for by the shift of the TS along the reaction co-ordinate. According to Achmatovicz and Szymoniak,⁴ the rate-constant change in the series of reactions of alkenes with DMMX is conditioned by the activation-energy change. Therefore, in accordance with the Hammond postulate, the decrease in activation energy causes the shift of TS along the reaction co-ordinate toward the reagents, *i.e.* for the late TS to the minimum of the volume profile, thus leading to the increase in $(-\Delta V^\ddagger)$. Unfortunately, as Zhulin²⁰ has shown, this hypothesis cannot explain his results for reactions with $a < 0$ and the early TS. Therefore a further study of this problem is required.

Let us now consider some consequences of eqn. (11). If we designate $\lg(k'/k'_{st})_{P=0}$ as $\hat{\sigma}$, then eqn. (12) holds.

$$\Delta V^\ddagger = \Delta V_{st}^\ddagger + a \cdot \hat{\sigma} \quad (12)$$

It is easy to show (see ref. 1) that eqn. (12) is equivalent to the existence of the linear dependence (13) that is formally an equation of the Hammett type. In this case a dependence in the

$$\lg k_p = \lg k_p^0 + \rho \cdot \hat{\sigma} \quad (13)$$

form of eqn. (4) should be observed. The result of our LSM calculations of ρ -values by means of eqn. (13) for reactions listed as entries 1–7 at 110 °C is presented in Fig. 5. The value of ρ is equal to $(5.43 \pm 0.65) \times 10^{-2} \text{ cm}^3 \text{ K}^{-1}$. Since [see above, after eqn. (9)] eqn. (14) holds, then the value of a will be equal to

$$a = \partial \Delta V_{\hat{\sigma}}^\ddagger / \partial \hat{\sigma} = -rT \quad (14)$$

-20.8 ± 2.5 . This does not significantly differ from the value obtained previously by eqn. (11).

The applicability of eqn. (11) allows us to draw some conclusions about the mechanism of ene reactions. This dependence has so far been found only for hydrogen-transfer

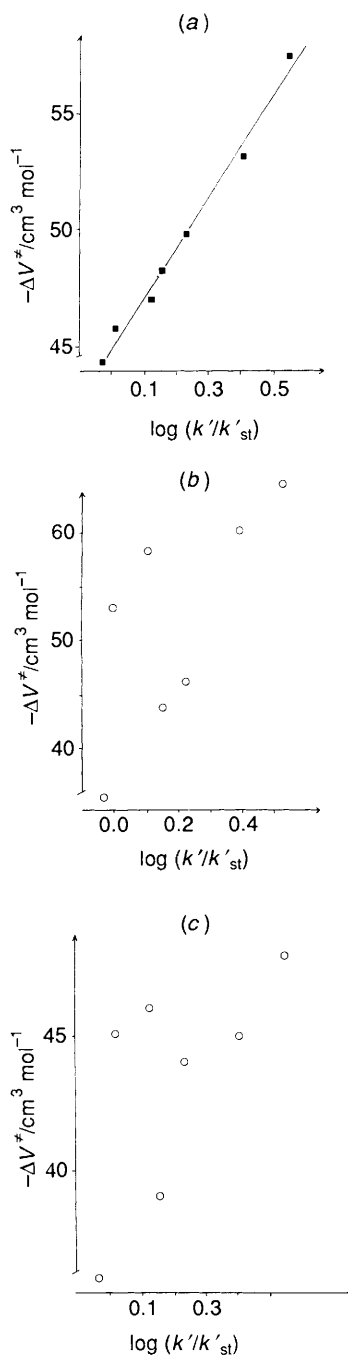


Fig. 4 Dependence of ΔV^\ddagger on $\lg k'/k'_{st}$ for reactions of alk-1-enes with DMMX (CCl_4 ; 110°C). Values of ΔV^\ddagger were evaluated with the help of: (a) eqn. (1), (b) eqn. (9), (c) graphically by eqn. (7).

reactions. It was not observed during the formation of carbon-carbon bonds in cycloaddition reactions²² or in radical additions to olefins.²⁰ Taking this into account we assign the existence of dependence [eqn. (11)] in ene reactions to the hydrogen-transfer step. This is one more piece of evidence (along with the above relationship $\Delta V^\ddagger/\overline{\Delta V} > 1$) in favour of a cyclic TS in these processes.

Most surprising is the fact that the formation of the carbon-carbon bond does not invalidate eqn. (11). As follows from the previous paragraph, in the series of reactions under comparison here an appreciable change in the activation volume increment due to this bond is not expected. However, in case the carbon-carbon bond is only partially formed in the TS, the change of degree of its formation in the series of reactions should contribute to the reaction-rate constant. Consequently, in this

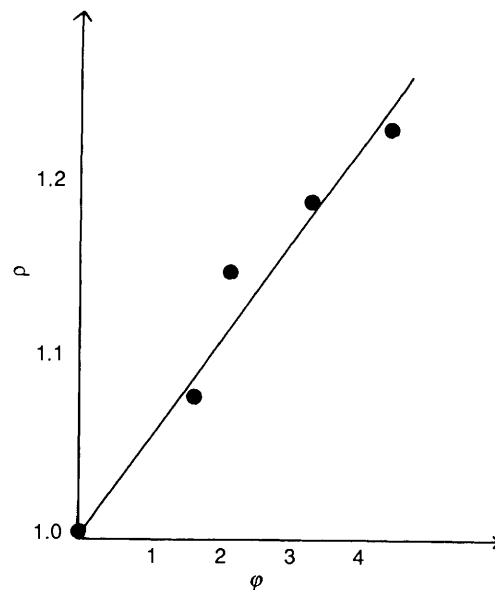


Fig. 5 Dependence of ρ on ϕ

case, dependence [eqn. (11)] is expected to be disturbed. Since this does not occur, we believe that formation of the carbon-carbon bond precedes to some extent the hydrogen-transfer step. In this sense the reaction is not exactly synchronous. The previously described⁴⁻⁹ distinctions might result from the change of rate-determining step.

Conclusions.—The ene reaction has been shown to be a process less concerted than cycloaddition, an observation also made by Fukui²³ with the help of theoretical calculations. We are aware that our conclusions, which do not strictly follow those gained with the help of other mechanistic arguments,⁴⁻⁸ rest on several (though reasonable) hypotheses and that they must be backed up with further kinetic data.

References

- 1 B. S. El'yanov, *Aust. J. Chem.*, 1975, **28**, 933.
- 2 B. S. El'yanov and E. M. Gonikberg, *J. Chem. Soc., Faraday Trans. 1*, 1979, **75**, 172.
- 3 B. S. El'yanov and E. M. Vasylytskaya, *Rev. Phys. Chem. Jpn.*, 1980, **50**, 169.
- 4 O. Achmatowicz, Jr. and J. Szymoniak, *J. Org. Chem.*, 1980, **45**, 1228.
- 5 W. A. Thaler and B. Franzus, *J. Org. Chem.*, 1964, **29**, 2226; R. Huisgen and H. Pohl, *Chem. Ber.*, 1960, **93**, 527.
- 6 G. Jenner and M. Papadopoulos, *J. Org. Chem.*, 1982, **47**, 4201.
- 7 R. Ben Salem and G. Jenner, *Tetrahedron Lett.*, 1986, **27**, 1575.
- 8 G. Jenner and R. Ben Salem, *Nouv. J. Chem.*, 1987, **11**, 677.
- 9 G. Jenner, R. Ben Salem, B. S. El'yanov and E. M. Gonikberg, *J. Chem. Soc., Perkin Trans. 2*, 1989, 1671.
- 10 B. S. El'yanov and E. M. Vasylytskaya, *Zh. Fiz. Khim.*, 1985, **59**, 264.
- 11 B. S. El'yanov, S. K. Shakova, B. D. Polkovnikov and L. F. Rar, *J. Chem. Soc., Perkin Trans. 2*, 1985, 11.
- 12 B. S. El'yanov and E. M. Gonikberg, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1987, 2464.
- 13 R. van Eldik, T. Asano and W. J. le Noble, *Chem. Rev.*, 1989, **89**, 549.
- 14 E. M. Vasylytskaya, B. S. El'yanov and V. M. Zhulin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1984, 2607.
- 15 G. A. Stashina, E. M. Vasylytskaya, G. D. Gamalevich, B. S. El'yanov, E. P. Serebryakov and V. M. Zhulin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1986, 329.
- 16 B. S. El'yanov, E. M. Vasylytskaya, V. M. Zhulin and M. Ya. Botnikov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1985, 1973.
- 17 T. Asano and W. J. le Noble, *Rev. Phys. Chem. Jpn.*, 1973, **43**, 82.
- 18 M. G. Gonikberg, V. M. Zhulin and B. S. El'yanov, in *The Physics and Chemistry of High Pressure*, Society of Chemical Industry, London, 1963, p. 212.
- 19 M. V. Basilevsky and N. N. Weinberg, *J. Mol. Liq.*, 1986, **33**, 1.

- 20 V. M. Zhulin, in *Organic High Pressure Chemistry*, ed. W. J. le Noble, Elsevier, Amsterdam, 1988 and references therein.
- 21 M. V. Basilevsky, N. N. Weinberg and V. M. Zhulin, *Int. J. Chem. Kinet.*, 1979, **11**, 853.
- 22 E. M. Vasylytskaya and B. S. El'yanov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1982, 2679.
- 23 S. Inagaki and K. Fukui, *J. Am. Chem. Soc.*, 1975, **97**, 7480, S. Inagaki, H. Fujimoto and K. Fukui, *J. Am. Chem. Soc.*, 1976, **98**, 46.

Paper 1/02781F

Received 10th June 1991

Accepted 6th September 1991