Oscillations of reactivity in the [2+4]-cycloaddition of methyl acrylate to furan

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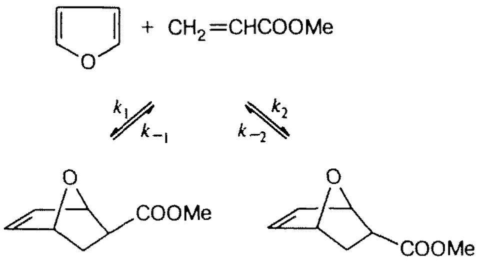
The kinetics of [2+4]-cycloaddition of methyl acrylate to furan (Diels—Alder reaction) were studied at 70 °C and 907 MPa, *i.e.*, under conditions where the solvent (benzene) exists in the solid state. It was found that the reactivity exhibits oscillations with astronomic time and that its averaging leads to reaction rate constants, which are close to those expected from the calculations, carried out using the known reaction and activation volume effects and the reactivity at a pressure close to the atmospheric pressure.

Key words: reactivity oscillations, Diels—Alder reaction, spline approximation.

Based on a study of the kinetics of [2+4]-cycloaddition of methyl acrylate (MA) to furan (F) (reaction (1)) at pressures of up to 98.1 MPa, we have proposed a hypothesis that the reactivity of substances changes periodically with time, no matter whether or not a particular process actually occurs.[1] Under the conditions mentioned above, this reaction is reversible and its rate is low. At the highest pressure of those used in the previous study (p = 98.1 MPa),[1] the equilibrium yield of adducts **1** + **2** is 30%, and at p = 2 MPa, it amounts to 10%. Therefore, in calculations of the kinetic parameters of the process, one should take into account the reverse reaction, *i.e.*, decomposition of the adduct, even in the initial section of the "[isomer]—time" ([Is]—τ) plot.



1 **2**

(1)

As the pressure increases, the rate of type (1) reactions substantially increases, and the equilibrium shifts toward the adducts.[2—4] Therefore, when the pressure is fairly high, the rate of the reverse reaction may be neglected until the degree of conversion is close to 100%.

In the range between 2.0 and 98.1 MPa, the period of the reactivity oscillations, which is equal to 10—20 h, did not change.[1] At a relatively high pressure, reaction (1) is so fast that its course can be followed over time intervals constituting only minor fractions of the period mentioned above. Thus, during a single time interval, *i.e.*, during a single experiment, the reactivity does not change. However, each subsequent experiment is carried out after a long period of time, measured in hours, and during this period the reactivity can markedly change. Consequently, a series of experiments carried out on different days provides a set of reactivities corresponding to various narrow sections of the period of the oscillations. This set is random and does not form a regular oscillatory dependence of reactivity on the reaction time either in amplitude or in the period of oscillations.

In order to verify our hypothesis,[1] in this work we studied the kinetics of reaction (1) at 70 °C and 907 MPa, *i.e.*, under conditions when the solvent (benzene) is solid.

Experimental

The experiments were carried out using a cylinder—piston type setup, according to a procedure similar to that described previously[5] except that the p values determined from the indication of a manometer, connected to a low-pressure chamber of a hydraulic press, were corrected, taking into account the multiplication coefficient, for the friction between the gaskets of the small piston and the walls of the high-pressure vessel; the experiments showed that these corrections amount to 7.5±2.5% of the p value.

Close to the specified value of p, the correction for friction was subtracted from the calculated p value. The pressure was continuously increased up to 10000 kg cm^{-2} and, after the correction for friction was introduced, it amounted to 907 MPa.

The temperature, equal to 70 °C, was maintained using an electric furnace and measured using a chromel to alumel thermocouple. The slight temperature difference between the

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 10, pp. 2450—2455, October, 1996.

Table 1. Degree of conversion (α) and the [**2**]/[**1**] isomer ratio during the period of the pressure increasing to the value p in reaction (1)

p/MPa	α	[**2**]/[**1**]
544	0.025	1.00
726	0.050	2.00
907	0.141	1.67
907*	0.160	2.07

Note. Reaction conditions: 70 °C; $[MA]_0$ = 0.1120, $[F]_0$ = 0.2292 mol.fr.* $[MA]_0$ = 0.0373; $[F]_0$ = 0.0786 mol.fr.

point where the thermocouple was located and the point where the Teflon ampule with the reaction mixture was located was determined with a mercury thermometer, which was placed into a tube with a high-boiling liquid situated inside the high-pressure apparatus but under atmospheric pressure.

The ampule with the reaction mixture was mounted into the conduit of a high-pressure sleeve, and at a slight compression (to prevent the contents from volatilization), it was heated to 70 °C over a period of 15 min. At pressures close to the atmospheric pressure, reaction (1) occurred slowly and reversibly; the yield of the adducts was 5—6% over a period of 6 h.

The pressure of 907 MPa was achieved over a period of 2.5 min, the time it took for pressure to increase from 544 to 907 MPa being equal to 30 s. During the increase in p at 70 °C, a noticeable amount of adducts was formed. Table 1 presents the overall yields of products and the ratios of isomers obtained in the experiments in which the pressure was increased to the value p at a constant temperature (70 °C), then the electric heating was immediately turned off, the furnace was removed, and p was reduced to atmospheric pressure over a period of a few seconds. The whole procedure, beginning with the switching-off of the electric heating and ending with the cooling of the ampule, required 2—3 min, so that the degrees of conversion (α) (in fractions of the initial concentration of MA), determined thereafter, and the ratios between the concentrations of isomeric products [**2**]/[**1**] corresponded exactly to the period during which the pressure was increased to p at 70 °C.

It can be seen from Table 1 that the α values determined for the two runs at 907 MPa are fairly close, although the initial concentrations of the starting compounds differ by a factor of three. This is due to the fact that the main bulk of benzene is frozen out under the experimental conditions and, hence, the initial concentrations in these reactions are equal. If we assume that benzene is entirely frozen out,* then the following concentrations should be used in the calculations of kinetic parameters: $[F]_0 = 0.6718$, $[MA]_0 = 0.3282$, and $[F]_0 = 0.6782$, $[MA]_0 = 0.3218$; these concentrations are rather close to one another and to those used in the previous study.[1]

At 70 °C, pure benzene freezes at ~260 MPa (as we estimated using the data of a previous study[6]). The pressures, at which the solution with the highest concentration used freezes and melts, were determined using the same setup by monitoring the displacement of the piston during the increase and decrease in p. The pressures at which the solution begins to freeze and begins to melt were found to be 522 and 474 MPa, respectively. Thus, reaction (1) occurred with the solvent separated in a solid phase.

Results and Discussion

Previously, in a study of 1,3-dipolar cycloaddition, it was found that the separation of a solvent, in particular benzene, in a solid phase markedly increases the reactivity of the compounds and its dependence on pressure,[7,8] and in the case of glycolisation, it even changes the ratio between the isomers formed.[9] Therefore, it was reasonable to find out whether similar effects take place in the case of [2+4]-cycloaddition.

For each of the two initial concentrations, 40 runs at normally 1-min intervals were carried out. Since benzene froze long before the pressure p = 907 MPa was achieved and the concentrations of the starting compounds became virtually identical, the series (40 runs each) can be considered to be parallel.

Using spline approximation of the "[Is]—τ" experimental points (Figs. 1 and 2), continuous d[Is]/dτ dependences were found. The scheme of reaction (1) is matched by the set of differential equations (2), where i = 1, 2.

$$d[Is]/d\tau = k_i[MA][F] - k_{-i}[Is] \qquad (2)$$

Since the rate constant k_{-i} of the reverse reaction (*i.e.*, for decomposition of the isomers) is small, the $W_i = \frac{1}{[MA][F]} \cdot \frac{d[Is]}{d\tau}$ value should be approximately equal to the rate constant of the forward reaction.

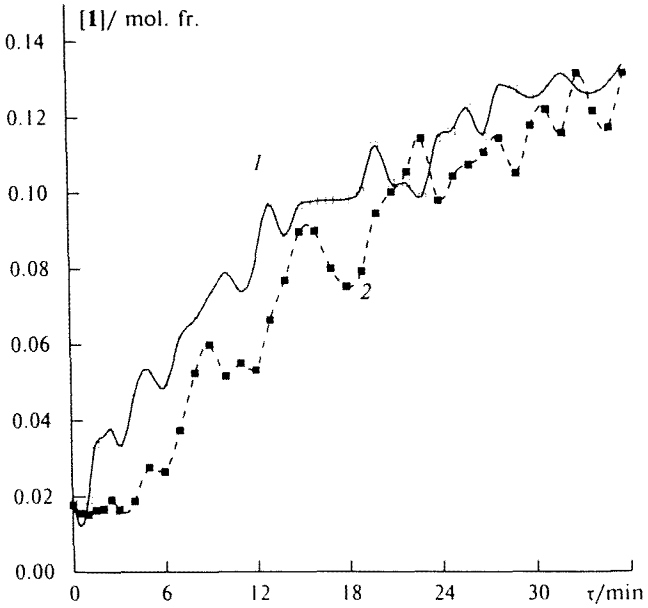


Fig. 1. Dependences of the concentration of **1** on the reaction time: experimental points obtained in the first series of experiments (*1*), experimental points obtained in the second series of experiments (*2*); p = 907 MPa, 70 °C; the curves were obtained by spline approximation with δ = 0.9995.

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* A small amount of benzene remains in the liquid phase.

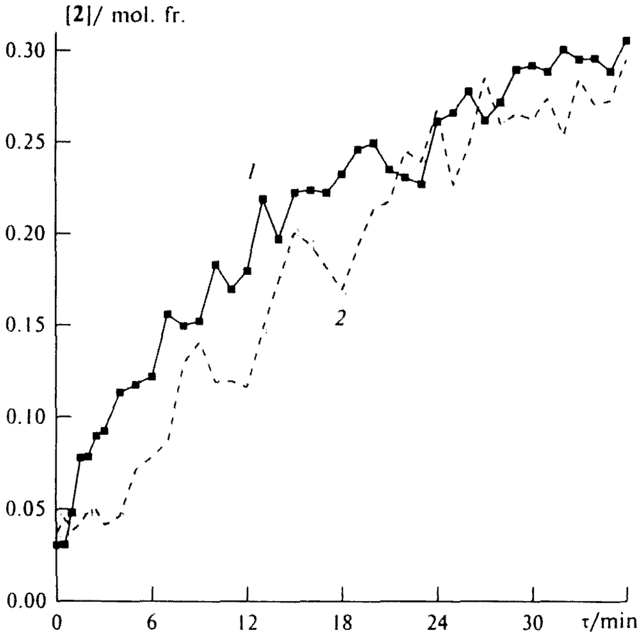

Fig. 2. Dependences of the concentration of **2** on the reaction time: experimental points obtained in the first series of experiments (*1*), experimental points obtained in the second series of experiments (*2*); p = 907 MPa, 70 °C; the curves were obtained by spline approximation with δ = 0.9995.

Figures 3 and 4 show the dependences of W_i for both series of experiments. The curves in Figs. 1—4 were drawn at δ = 0.9995 (this is the parameter characterizing the ratio between the accuracy and the smoothness of an approximation; for more detail, see Ref. 1). The δ value varies in the 0—1 range; the larger δ, the more accurately the curve passes through the points, but simultaneously, it becomes less smooth. At δ = 0.9995, the curves pass through the points with almost the highest degree of accuracy and with the lowest smoothness.

The plots shown in Figs. 1—4 indicate that the reactivity has changed; therefore, in the subsequent calculations and comparisons, we used the average values of the reaction rate constants, which were found by two methods: as the arithmetic mean k_{in} (Eq. (3)) over n points arranged at equal distances along the τ axis, and as the integral mean value $k_{i\tau}$ (Eq. (4)):

$$k_{in} = \frac{1}{n} \cdot \sum_{j=1}^{n} W_{ij}, \qquad (3)$$

$$k_{i\tau} = \frac{1}{\tau_2 - \tau_1} \cdot \int_{\tau_1}^{\tau_2} W_i(t)\mathrm{d}t. \qquad (4)$$

We analyzed the effect of the δ value on k_{in} at n = 201; for this purpose, k_{in} was calculated at 40 values of δ ranging from 0 to 1 with a step of 0.025. It was found that in the first series of experiments, as δ increases to 0.925, the k_{1n} value increases from 0.045 to 0.050 mol. fr.$^{-1}$ min^{-1} and then decreases to 0.049, *i.e.*, it changes only by 10% and, on the average, amounts to 0.047. The

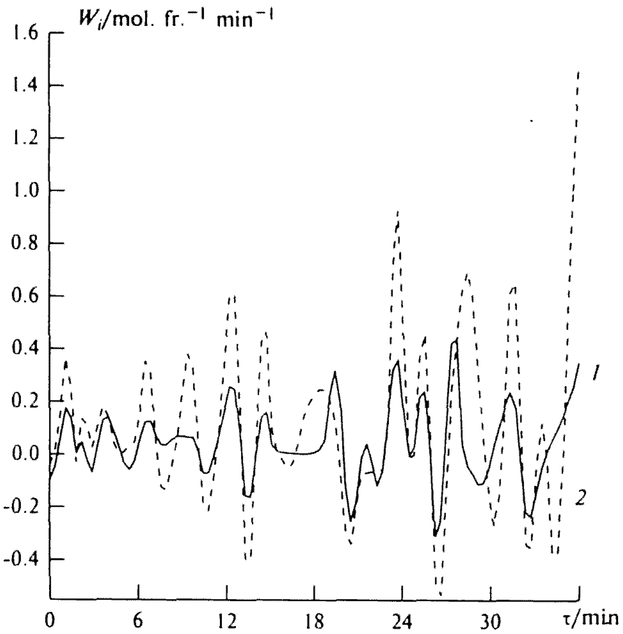

Fig. 3. Dependences of $W_i = \frac{1}{[\mathrm{MA}][\mathrm{F}]} \cdot \mathrm{d}[\mathrm{Is}]/\mathrm{d}\tau$ on the reaction time in the first series of experiments: *1*, i = 1 (**1**); *2*, i = 2 (**2**).

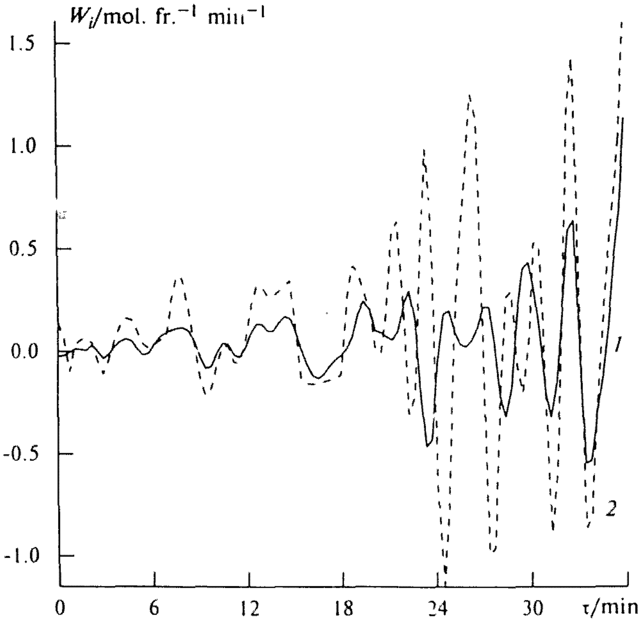

Fig. 4. Dependences of $W_i = \frac{1}{[\mathrm{MA}][\mathrm{F}]} \cdot \mathrm{d}[\mathrm{Is}]/\mathrm{d}\tau$ on the reaction time in the second series of experiments: *1*, i = 1 (**1**); *2*, i = 2 (**2**).

Table 2. The k_{in} and $k_{i\tau}$ values (mol.fr.$^{-1}$ min^{-1}) at various δ

δ	k_{1n}	k_{2n}	$k_{1\tau}$	$k_{2\tau}$
		Series 1		
0.2	0.046	0.105	0.045	0.104
0.4	0.047	0.107	0.045	0.106
0.6	0.048	0.110	0.047	0.109
0.8	0.049	0.114	0.048	0.109
		Series 2		
0.2	0.043	0.097	0.043	0.096
0.4	0.044	0.100	0.043	0.098
0.6	0.046	0.103	0.043	0.099
0.8	0.049	0.108	0.046	0.096

Note. Conditions: p = 907 MPa, 70 °C, n = 201, τ_1 = 0 min, τ_2 = 36 min.

dependence of k_{2n} on δ has a minimum at δ = 0.1, and the whole change in k_{2n} is 21%, its average value being equal to 0.110.

In the second series of experiments, the k_{1n} value changes by 36%, and its average value (over the same 40 points) is 0.46; k_{2n} increases from 0.092 to 0.121 over the whole range of variation of δ and, on the average, it is equal to 0.103.

Thus, the k_{in} values in the two series of experiments differ by no more than 7%. Comparison of the k_{in} and $k_{i\tau}$ values presented in Table 2 for several δ shows that at identical i, these values are equal.

To find out whether k_i obtained agree with the actual values, we used the data presented in a known paper[1] and relation (5) (see Ref. 10):

$$RT\ln(k_p/k_0) = -\Delta V_0^{\neq}\cdot[(1+\alpha)p - (\alpha/\beta)\cdot(1+\beta p)\cdot\ln(1+\beta p)], \quad (5)$$

where k_p and k_0 are the rate constants for the reaction at pressure p and at atmospheric pressure, respectively; $\Delta V_0^{\neq}$ is the activation volume effect at atmospheric pressure; α and β are empirical coefficients; for the Diels—Alder reaction they are equal to 0.170 and $4.94\cdot10^{-3}$ bar^{-1}, respectively.[10]

Using the previously obtained[1] values of k_{in} (n = 25, δ = 0.4) for 2 MPa, the average $\Delta V_i^{\neq}$ values for the p = 2.0—98.1 MPa range, and Eq. (5), we obtain k_{1n} = $1.05\cdot10^{-4}$ and k_{2n} = $2.44\cdot10^{-4}$ mol.fr.$^{-1}$ min^{-1} for atmospheric pressure. A similar calculation for p = 907 MPa carried out using the same data and the values $\Delta V_0^{\neq}$ = −37.4 cm^3 mol^{-1} for **1** and $\Delta V_0^{\neq}$ = −36.3 cm^3 mol^{-1} for **2** (see Ref. 1) yields the results k_{1n} = 0.043 mol.fr^{-1} min^{-1} and k_{2n} = 0.083 mol.fr^{-1} min^{-1}, which do not differ too much from the corresponding values given in Table 2.

A somewhat different approach to the estimation of the agreement of the results obtained in the present study with those obtained previously[1] involves the use of a linear correlation for free energies:[10]

$$\log(k_p/k_0) = -(\Delta V_0^{\neq}/T)\cdot\Phi, \quad (6)$$

$$\Phi = [(1+\alpha)p - (\alpha/\beta)\cdot(1+\beta p)\cdot\ln(1+\beta p)]/R\ln10. \quad (7)$$

This makes it possible to determine $\Delta V_0^{\neq}$ and k_0 by the least-squares method from the $\log k_p$—p experimental dependence.

Equations (6) and (7) are also applicable to the equilibrium constants (K_{eq}); in this case, instead of the activation volume effect, the calculation yields the reaction volume effect (ΔV_0) (the change in volume during the reaction).

Table 3 presents the values of k_0, K_0, $\Delta V_0^{\neq}$, and ΔV_0, which were calculated from the published data,[1] resorting to the k_i values for p = 907 MPa obtained in the first and in the second series of experiments, respectively, and using the equilibrium constants $K_i = k_i/k_{-i}$, where k_i and k_{-i} are the average values, and K_{eq} = [Is]/([MA][F]), averaged over the two values obtained for the forward and reverse reactions at a maximum reaction time of 50 h (see Table 1 in Ref. 1). It can be seen from Table 3 that the rate and equilibrium constants differ by no more than 15%, $\Delta V_0^{\neq}$ differ by no more than 18%, and the ΔV_0 values differ by no more than 21%.

It is believed that the most accurate values for $\Delta V_0^{\neq}$ and ΔV_0 have been obtained for the Diels—Alder reaction between isoprene and maleic anhydride at 35 °C in various solvents;[11] ΔV_0 varies from −30.7 to −38.3, while $\Delta V_0^{\neq}$ varies from −32.5 to −39.8 cm^3 mol^{-1}. The ΔV_0 value for reaction (1), calculated from the densities of the mixtures of the reaction products and initial compounds, is −30.0 cm^3 mol^{-1}.[5] According to a known rule,[10] when the temperature increases by 1°, the magnitude of ΔV increases by 0.5%, which leads to ΔV_0 = −30.7 cm^3 mol^{-1} for reaction (1) at 35 °C. The same ΔV_0 value has been found[11] for the reaction of isoprene with maleic anhydride in nitromethane. If we assume that the $\Delta V_0^{\neq}$ values for these reactions are also identical and are equal to −32.5 cm^3 mol^{-1} (see Ref. 11), then, in conformity with the above-mentioned rule, for the reac-

Table 3. Rate and equilibrium constants and activation and reaction volume effects at 70 °C under atmospheric pressure

$k_1\cdot10^4$	$k_2\cdot10^4$	$-\Delta V_1^{\neq}$	$-\Delta V_2^{\neq}$	K_1	K_2	$-\Delta V_1$	$-\Delta V_2$
mol.fr.$^{-1}$ min^{-1}		cm^3 mol^{-1}		mol.fr.$^{-1}$		cm^3 mol^{-1}	
1.09	2.46	44.2±5.3	43.7±5.4	0.098	0.087	46.5±4.1	47.5±4.8
1.20	2.67	37.5±0.9	37.8±0.9	0.102	0.095	38.3±2.5	42.2±5.8
1.21	2.69	37.1±0.9	37.3±0.9				

Table 4. Kinetic parameters $k_{i\tau}$ (mol.fr.$^{-1}$ min^{-1}) for reaction (1) (averaged over each of the eight 4.5 min intervals beginning from $\tau = 0$ with a curve with $\delta = 0.8$)

Interval	$k_{1\tau}$	$k_{2\tau}$	$k_{1\tau}$	$k_{2\tau}$
	Series 1		Series 2	
1	0.046	0.119	0.007	0.024
2	0.048	0.085	0.053	0.115
3	0.050	0.120	0.031	0.059
4	0.024	0.096	0.013	0.041
5	0.010	−0.013	0.106	0.225
6	0.099	0.175	0.011	0.128
7	0.065	0.198	0.066	−0.008
8	0.041	0.089	0.079	0.182

tion under consideration at 70 °C, we obtain $\Delta V_0^{\ne} = -38.2$ cm^3 mol^{-1}. A similar calculation of ΔV_0 at 70 °C yields −36.1 cm^3 mol^{-1}. The latter ΔV_0 and $\Delta V_0^{\ne}$ values differ only slightly from those presented in Table 3, if we take into account the values of errors given in the same Table.

Calculations show that the magnitudes of the rate constants of the reactions for both isomers, calculated with the assumption that the k_{-i} values in Eq. (2) are small and averaged in the 0—36 min range, correspond to the expected values.

To estimate the second term in the right-hand side of Eq. (2), we used the following activation volume effects for the decomposition of isomers: $\Delta V^{\ne}_{-1} = 1.9$ and $\Delta V^{\ne}_{-2} = 3.8$ cm^3 mol^{-1}; the average of these two values is $\Delta V^{\ne}_{-i} = 2.9$ cm^3 mol^{-1}. As an estimation of the rate constants for the decomposition of the isomers under atmospheric pressure, we took the values obtained previously[1] for $p = 2$ MPa. Then the decomposition rate constants for $p = 907$ MPa can be found from the empirical equation (5) reported previously,[12] which relates the rate constants k_0 and k_p and activation volume effects of decomposition to the p value, similarly to Eq. (5) given in this paper. This yields $k_{-1} = 4.9 \cdot 10^{-4}$ and $k_{-2} = 13.2 \cdot 10^{-4}$ min^{-1}, *i.e.*, values that are only half those found for $p = 2$ MPa.

For a yield of the isomers of 56% ($\tau = 9$ min), the k_{-1} [**1**]/([MA][F]) and k_{-2} [**2**]/([MA][F]) values are 0.7% and 1.7% of W_1 and W_2. When the degree of conversion is 93% ($\tau = 36$ min), these percentages increase to 8 and 22, respectively. Therefore, it might be expected that the k_i values for the first half of the 36-minute reaction period would be larger than those for the second half of this period, where the rate of the decomposition of isomers becomes higher. However, the calculation of the average rate constants $k_{i\tau}$ (at $\delta = 0.8$) in the 0—18 and 18—36 min intervals resulted in $k_1 = 0.042$ and 0.054, and $k_2 = 0.105$ and 0.112 mol.fr.$^{-1}$ min^{-1} for the first series of experiments, and $k_1 = 0.026$ and 0.065, and $k_2 = 0.059$ and 0.132 mol.fr.$^{-1}$ min^{-1} for the second series of experiments.

Thus, in the second time interval, the average rate constants increase rather than decrease, which is especially pronounced in the second series of experiments. This result confirms the hypothesis that the reactivity undergoes oscillations with astronomic time: the second interval of the reaction period happened to contain those sections of the oscillation period, which correspond to higher average $k_{i\tau}$ than the sections that fell within the first interval.

Table 4 presents the $k_{i\tau}$ values for shorter time intervals, $\tau = 4.5$ min. The $\tau = 36$ min period consists of eight such intervals. The slightly negative $k_{i\tau}$ values as well as the relatively large negative W_i cannot be interpreted as indicating that decomposition predominates during these intervals (see Figs. 3 and 4). These negative values merely indicate that the specific rate of the reaction is lower than that in an interval (or at a point) where the $W_{i\tau}$ (W_i) value is positive or less negative.

It can be seen from Table 4 that the smallest $k_{i\tau}$ values can actually be found during the second half of the reaction period (intervals 5 and 7), but the largest $k_{i\tau}$ values are also encountered there.

As noted above, in the general case, the dependence of W_i on τ is not necessarily regular. Nevertheless, it can be seen that the spaces between the "peaks" are quite close in size (see Figs. 1—4). This can be explained by the fact that there was a certain order in conducting the experiments. As a rule, 4—5 runs involving the same mixture of the initial compounds were pursued every day at intervals of 1—1.5 h. From the known number of spaces between the rate maxima (or minima) and the number of experiments conducted over the whole course of the reaction, the period of oscillations can be esti-

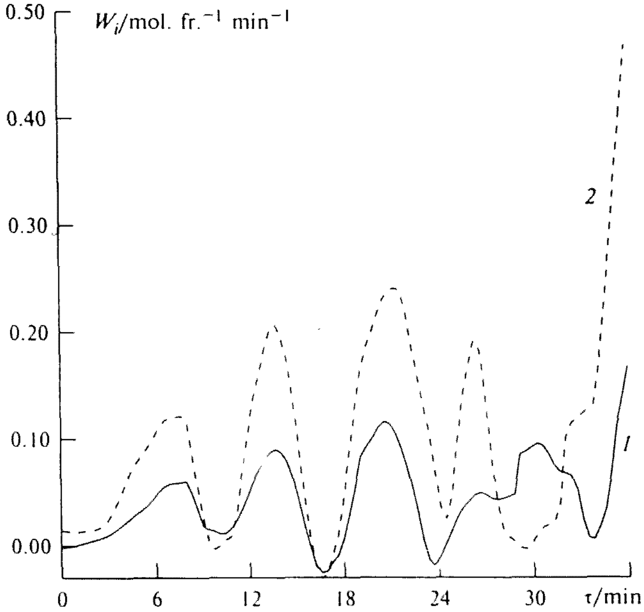

Fig. 5. Dependences of $W_i = \frac{1}{[\mathrm{MA}][\mathrm{F}]} \cdot \mathrm{d[Is]/d}\tau$ on the reaction time obtained by differentiating the "[Is]—τ" spline curves ($\delta = 0.4$) in the second series of experiments: *1*, $i = 1$ (**1**); *2*, $i = 2$ (**2**).

mated. The curves shown in Figs. 1—2 pass through the experimental points too exactly. Therefore, their derivatives (see Figs. 3—4) may contain peaks arising not only due to the reactivity oscillations but also due to random errors of the experiment. By considering similar plots obtained for $\delta = 0.8$ to 0.05, one may conclude that in this range of δ, the number of peaks does not vary and is equal to 4—5 (the "shoulders" are not included). Let us assume that the number of spaces between the peaks is 5; since 40 runs correspond to this number, each interval includes 8 runs, *i.e.*, 8—12 h. Although this evaluation of the oscillation period is rough, it indicates that it is of the same order of magnitude as the periods calculated previously[1] for $p = 2.0{-}98$ MPa. Figure 5 shows the corresponding dependences obtained for the same δ value ($\delta = 0.4$) as in the previous study.[1]

The data presented confirm that the reactivity undergoes oscullations with time. The regular character of these oscillations is most likely due to the fact that the experiments were conducted with a certain orderliness in astronomic time.

The occurrence of the reactivity oscillations in astronomic time is also indicated by the oscillations of the kinetic characteristics of some radical reactions, occurring as the degree of conversion increases, as well as by the unusual pressure dependences of the activation volume effects that we have observed previously.[13—16]

The averaging of the specific rates of the formation of the isomers, obtained as continuous plots by spline approximation of the "Is—τ" data, affords values of reaction rate constants close to those expected at 907 MPa and 70 °C. This result, in turn, suggests that the presence of a solvent as a solid phase has no effect on the reactivity: the reaction occurs in the separated liquid macrophase consisting of the mixture of methyl acrylate and furan that does not freeze under these conditions.[5] The relative amount of the liquid microphase, in which kinetic parameters of the reaction can change, may be rather small under these conditions.

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Received April 23, 1996