Determination of heats of the thermal gas-phase formation of intermediates with overlapping spectra

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The previously proposed procedure for the determination of heats of thermal gas-phase reversible reactions using kinetic spectroscopy was extended for the case of the formation of two intermediate species with overlapping UV spectra. The model problem was solved, and the error of the method was estimated. Applicability of the method was shown for the reversible formation of trimethylenemethane (TMM) and but-1-ene-2,4-diyl from methylenecyclopropane.

Key words: pyrolysis, intermediates, enthalpies of reactions, adiabatic compression; kinetic spectroscopy.

Previously the adiabatic compression method combined with kinetic UV spectroscopy has been successfully used for the detection of short-lived intermediate species and determination of the detailed mechanism of the gas-phase reactions.[1-5] A new method for the determination of heats of thermal gas-phase reactions of the formation of intermediates has been recently suggested.[6] In this method, the equilibrium concentration expressed from the Bouguer—Lambert—Beer law is equalized to the concentration of the intermediate determined by the product of the equilibrium constant and the concentration of the starting compound. The formula for the calculation is obtained by the transformation of this equality with separation of the enthalpy term of the equilibrium constant. The method suggested[6] has been used for the determination of the enthalpy of the formation of the $^{\cdot}CF_2-^{\cdot}CF_2$ biradical.

However, the spectral pattern is often more complicated when the conversion and/or temperature increase. The most complicated is the situation when spectra of two and more intermediates overlap. This gives rise to difficulties for processing kinetic spectral data, determination of the enthalpy of formation of the intermediates, and calculation of kinetic schemes.

The purpose of this study is to develop a method for the determination of heats of reversible reactions of the formation of two intermediates in the case of overlapping absorption bands, illustrate the possibilities of the method using a model problem, and apply it to a particular experiment.

Physicochemical fundamentals of the method

The approach considered is adapted to a combination of the adiabatic compression method and kinetic spectroscopy. However, it also can be used in other cases when the main assumptions accepted previously[6] are fulfilled.

The physicochemical fundamentals of the "adiabatic compression/kinetic spectroscopy" method have been considered in several works.[2,7,8] Experimental data obtained by this method are changes in time of the light absorption and pressure of the reacting mixture. The examples of the typical computer recording of these values are presented in Fig. 1, *a*, *b*. In addition, the maximum value of the geometrical compression degree $\varepsilon_{max} = V_0/V_{min}$ (V_0 and V_{min} are the gas volume before compression and at the moment of the piston halt, respectively) is measured.[7] This value is achieved at the moment of the piston halt (t_0). It is accepted in Fig. 1, *a*, *b* that $t_0 \equiv 0$, and the t values are read off from this point.

The main conditions of applicability of the method are retained for the determination of heats of thermal gas-phase reversible reactions of the formation of two intermediates:[6] 1. The concentration of the intermediates is equilibrium at the moment of the maximum compression t_0. 2. The equilibria in the reactions of the formation of the intermediates should not be distorted by other processes involving these intermediates. In the other words, the rates of the reverse reactions should be substantially higher than the overall rate of the decay of the intermediates *via* other routes.

The experimental conditions are specified in such a way that the number of moles of the starting compound remains almost unchanged during the compression—expansion cycle.

In terms of the adiabatic compression method, changes in the temperature and pressure obey the equations of the Poisson adiabatic curve, and the maximum

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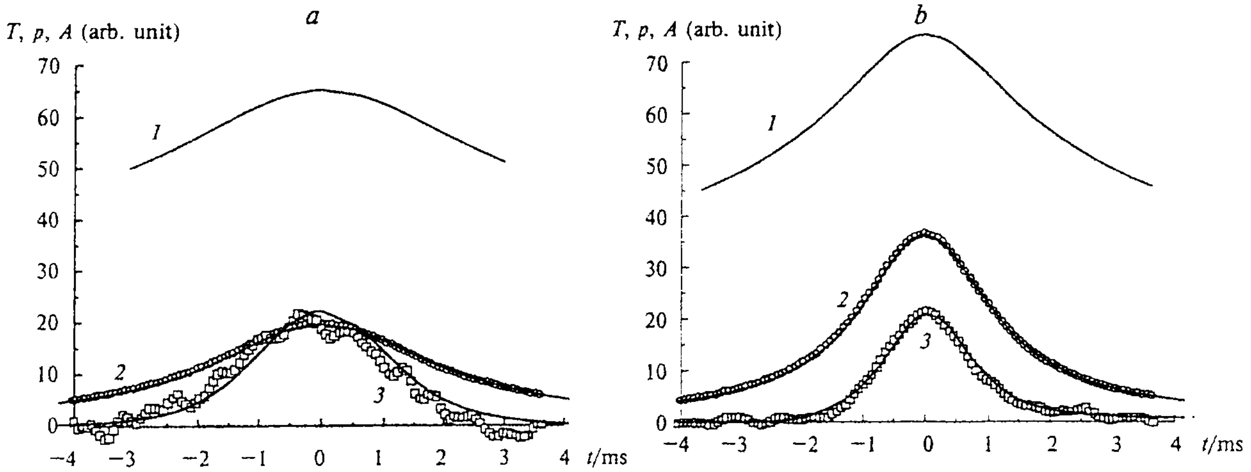

Fig. 1. Changes in time of the temperature, $T\cdot 10^{-1}$/K (*1*); pressure, p/atm (*2*); and light absorption, A (%) (*3*) on adiabatic heating of the system to T_{max} = 654 K; λ = 237.5 nm (*a*) and T_{max} = 754 K; λ = 247.5 nm (*b*) (points are experiment, solid lines are calculation).

temperature is achieved at the maximum compression moment in a mixture of reagents strongly dilute with an inert gas. At the known pressure and volume ($V_{min} = V_0/\varepsilon_{max}$), the maximum temperature is determined from the equation of state.

Let us consider four typical processes of the formation of intermediates I_1 and I_2 from the starting compound A:

— *parallel*

$$A \rightleftharpoons I_1,\ A \rightleftharpoons I_2; \qquad (1)$$

— *simple consecutive*

$$A \rightleftharpoons I_1 \rightleftharpoons I_2; \qquad (2)$$

— *consecutive with branching*

$$A \rightleftharpoons I_1 \rightleftharpoons 2\,I_2, \qquad (3)$$

$$A \rightleftharpoons I_1 \rightleftharpoons I_2 + B, \qquad (4)$$

where B is the stable reaction product.

At the moment of maximum compression (t_0), the Bouguer—Lambert—Beer equations of the light absorption by the intermediates can be written in the following form:

$$-\ln\left\{1-\frac{\Delta J(t_0)}{J_0}\bigg|_{\lambda_j}\right\} = D^{\Sigma}_{\lambda_j} = (\sigma_{1,\lambda_j}C_{1,eq} + \sigma_{2,\lambda_j}C_{2,eq})l =$$
$$= D^{(1)}_{\lambda_j} + D^{(2)}_{\lambda_j}, \qquad (5)$$

where $\Delta J(t_0) = J_0 - J(t_0)$; J_0 and J are the intensities of the incident light and the light transmitted through the gas under study, respectively; σ_i,λ_j is the extinction coefficient of the ith intermediate at the jth wavelength (j = 1, 2); $C_{i,eq}$ is the equilibrium concentration of the ith intermediate; l is the thickness of the gas layer absorbing the light; and $D_{\lambda_j}{}^{\Sigma}$ is the experimental (total) optical density.

For processes (1)—(4), the equilibrium concentrations of the intermediates $C_{i,eq}$ at the t_0 moment are determined by the following thermodynamic correlations (hereinafter the numbers of the corresponding equations are given in parentheses):

$$C_{1,eq}(1-4) = K_{1,eq}\cdot M/V_{min} =$$
$$= A_1\exp[-\Delta Q_1/(RT_{max})]M\varepsilon_{max}/V_0; \qquad (6)$$

$$C_{2,eq}(1) = K_{2,eq}\cdot M/V_{min} =$$
$$= A_2\exp[-\Delta Q_2/(RT_{max})]M\varepsilon_{max}/V_0; \qquad (7)$$

$$C_{2,eq}(2) = K_{2,eq}C_{1,eq} = K_{2,eq}K_{1,eq}M/V_{min} =$$
$$= A_1A_2\exp[-(\Delta Q_1 + \Delta Q_2)/(RT_{max})]M\varepsilon_{max}/V_0; \qquad (8)$$

$$C_{2,eq}(3,\,4) = (K_{2,eq}C_{1,eq})^{1/2} = (K_{2,eq}K_{1,eq}M/V_{min})^{1/2} =$$
$$= \{A_1A_2\exp[-(\Delta Q_1 + \Delta Q_2)/(RT_{max})]M\varepsilon_{max}/V_0\}^{1/2}, \qquad (9)$$

where $K_{i,eq}$ is the equilibrium constant of the formation of the ith intermediate, A_i is its entropy term, ΔQ_i is the heat, M is the number of moles of the starting compound. For process (4), $C_{2,eq}(4) = C_B$.

Expressing the concentration of the intermediate $C_{1,eq}$ from Eqs. (5) and (6) and equalizing the correlations obtained, we have

$$\frac{\sigma_{2,\lambda_2}D^{\Sigma}_{\lambda_1} - \sigma_{2,\lambda_1}D^{\Sigma}_{\lambda_2}}{(\sigma_{1,\lambda_1}\sigma_{2,\lambda_2} - \sigma_{1,\lambda_2}\sigma_{2,\lambda_1})l} =$$
$$= (A_1M\varepsilon_{max}/V_0)\exp[-\Delta Q_1/(RT_{max})],$$

from where

$$\ln\frac{(\sigma_{2,\lambda_2}D^{\Sigma}_{\lambda_1} - \sigma_{2,\lambda_1}D^{\Sigma}_{\lambda_2})V_0}{(\sigma_{1,\lambda_1}\sigma_{2,\lambda_2} - \sigma_{1,\lambda_2}\sigma_{2,\lambda_1})lM\varepsilon_{max}} = \ln A_1 - \Delta Q_1/(RT_{max}). \qquad (10)$$

Similarly, correlations for the second intermediate can be obtained from Eqs. (5) and (7)—(9). Here l and V_0

are the parameters of the experimental setup, and M is determined from the original values of the pressure, temperature, and composition of the gas under study. The light absorption is measured in a series of experiments at different $\varepsilon_{\max}$ (correspondingly, $T_{\max}$).

The left part of Eq. (10) contains unknown magnitudes: σ_{1,λ_1}, σ_{1,λ_2}, σ_{2,λ_1}, and σ_{2,λ_2}. UV spectroscopic data can give the following ratios: $\sigma_{1,\lambda_2}/\sigma_{1,\lambda_1} = \alpha_1$ and $\sigma_{2,\lambda_1}/\sigma_{2,\lambda_2} = \alpha_2$, where λ_1 and λ_2 are the wavelengths corresponding to the maxima of the absorption bands* of intermediates I_1 and I_2. Then we can write

$$\frac{\sigma_{2,\lambda_2} D^{\Sigma}_{\lambda_1} - \sigma_{2,\lambda_1} D^{\Sigma}_{\lambda_2}}{\sigma_{1,\lambda_1}\sigma_{2,\lambda_2} - \sigma_{1,\lambda_2}\sigma_{2,\lambda_1}} = \frac{\sigma_{2,\lambda_2}(D^{\Sigma}_{\lambda_1} - \alpha_2 D^{\Sigma}_{\lambda_2})}{\sigma_{1,\lambda_1}\sigma_{2,\lambda_2}(1-\alpha_1\alpha_2)} =$$

$$= \frac{D^{\Sigma}_{\lambda_1} - \alpha_2 D^{\Sigma}_{\lambda_2}}{\sigma_{1,\lambda_1}(1-\alpha_1\alpha_2)}$$

and present Eq. (10) in the following form:

$$Z_1(1\text{—}4) \equiv \ln\frac{(D^{\Sigma}_{\lambda_1} - \alpha_2 D^{\Sigma}_{\lambda_2})V_0}{(1-\alpha_1\alpha_2)lM\varepsilon_{\max}} =$$

$$= \ln(\sigma_{1,\lambda_1}A_1) - \Delta Q_1/(RT_{\max}). \tag{11}$$

Similarly,

$$Z_2(1) \equiv \ln\frac{(D^{\Sigma}_{\lambda_2} - \alpha_1 D^{\Sigma}_{\lambda_1})V_0}{(1-\alpha_1\alpha_2)lM\varepsilon_{\max}} =$$

$$= \ln(\sigma_{2,\lambda_2}A_2) - \Delta Q_2/(RT_{\max}), \tag{12}$$

$$Z_2(2) \equiv \ln\frac{(D^{\Sigma}_{\lambda_2} - \alpha_1 D^{\Sigma}_{\lambda_1})V_0}{(1-\alpha_1\alpha_2)lM\varepsilon_{\max}} =$$

$$= \ln(\sigma_{2,\lambda_2}A_1A_2) - (\Delta Q_1 + \Delta Q_2)/(RT_{\max}), \tag{13}$$

$$Z_2(3,\ 4) \equiv 2\ln\frac{D^{\Sigma}_{\lambda_2} - \alpha_1 D^{\Sigma}_{\lambda_1}}{(1-\alpha_1\alpha_2)l} + \ln\frac{V_0}{M\varepsilon_{\max}} =$$

$$= \ln(\sigma^2_{2,\lambda_2}A_1A_2) - (\Delta Q_1 + \Delta Q_2)/(RT_{\max}). \tag{14}$$

The left part of Eqs. (11)—(14) now contains only the magnitudes determined experimentally. Then the ΔQ_1 and ΔQ_2 values can be determined by plotting the dependences of Z_1 and Z_2 on $1/(RT_{\max})$ for experiments with different $\varepsilon_{\max}$.

Determination of λ_2, α_1, and α_2 from experimental data

Sufficiently exact determination of the aforementioned values is necessary to apply the method. The typical sequence of the procedures used is presented below.

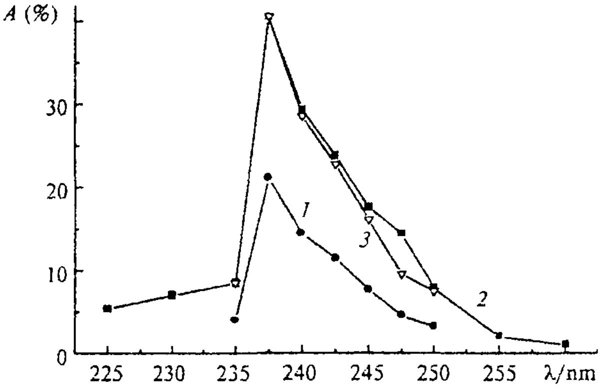

Fig. 2. Absorption spectra upon adiabatic heating of the mixture: *1*, $T_{\max}$ = 654 K (TMM, experiment); *2*, $T_{\max}$ = 710 K (TMM + but-1-ene-2,4-diyl, experiment); *3*, $T_{\max}$ = 710 K (TMM, calculation).

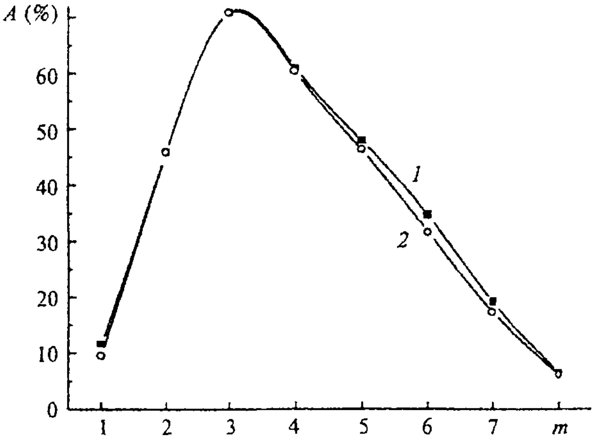

Fig. 3. Calculated absorption spectra in the solution of the model problem (18) for $T_{\max}$ = 901 K: *1*, total; *2*, of the intermediate I_1.

The lowest temperature, at which the UV spectrum of the first intermediate I_1 can be obtained, is established, and the spectrum is recorded. The λ_1 value is determined from this spectrum. Then the absorption spectra at higher temperatures are recorded. If they are similar, the other intermediates (even if any) are accepted not to absorb in this spectral range. Let us consider a more complicated situation when an increase in the temperature changes the spectral pattern: a "shoulder" appears and half-widths of absorption bands change (usually increase) (Figs. 2 and 3). This implies the presence of one more intermediate, whose absorption spectrum overlaps the spectrum of I_1. In several cases, the appearance of the second intermediate I_2 also can be seen from the time dependence of the light absorption (see below).

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* The approach to the experimental determination of the λ values is given below.

In the temperature range, in which the aforementioned properties of the appearance of I_2 have not yet been detected, the time dependences of the pressure and light absorption are obtained for different T_{max} at the λ_1 wavelength. The ΔQ_1 and $\sigma_{1,\lambda_1}A_1$ values are determined from these data according to the previously presented procedure.[6]

The error of determination of ΔQ_1 depends on the temperature range and number of experimental points. Until the linear $Z_1 = Z_1[1/(RT_{max})]$ dependence is distorted while being continued to the high-temperature region, the contribution of the second intermediate to the light absorption at the λ_1 wavelength can be neglected, which was checked by computer simulation.

Let us calculate the relative extinction coefficients (β_m) at different λ_m wavelengths for the first intermediate from the absorption spectrum of I_1:

$$\beta_m = \frac{\sigma_{1,\lambda_m}}{\sigma_{1,\lambda_1}} = \frac{\sigma_{1,\lambda_m}C_{1,eq}l}{\sigma_{1,\lambda_1}C_{1,eq}l} = \frac{D^{(1)}_{\lambda_m}}{D^{(1)}_{\lambda_1}} \approx \frac{D^{\Sigma}_{\lambda_m}}{D^{\Sigma}_{\lambda_1}} \; . \qquad (15)$$

It should be noted that when $\lambda_m = \lambda_2$, $\beta_m = \alpha_1$. Using the obtained β_m, ΔQ_1, and $\sigma_{1,\lambda_1}A_1$ values, we can calculate the light absorption caused by I_1 in the case when I_2 is knowingly present. The calculated and total (experimental) light absorptions are compared, and the wavelength, at which the difference between them is maximum, is determined. This is λ_2 (see Figs. 2 and 3).

Then the time dependences of the pressure and light absorption for different T_{max} values are determined at the λ_2 wavelength. The experimental results with the lowest T_{max} are used for the calculation of α_1:

$$\alpha_1 = \frac{\sigma_{1,\lambda_2}}{\sigma_{1,\lambda_1}} = \frac{D^{(1)}_{\lambda_2}}{D^{(1)}_{\lambda_1}} \approx \frac{D^{\Sigma}_{\lambda_2}}{D^{\Sigma}_{\lambda_1}} \; . \qquad (16)$$

To calculate α_2, Eq. (5) should be transformed:

$$\frac{D^{\Sigma}_{\lambda_2} - \sigma_{1,\lambda_2}C_{1,eq}l}{\sigma_{2,\lambda_2}l} = C_{2,eq} = \frac{D^{\Sigma}_{\lambda_1} - \sigma_{1,\lambda_1}C_{1,eq}l}{\sigma_{2,\lambda_1}l} \; ,$$

from where

$$\alpha_2 = \frac{\sigma_{2,\lambda_1}}{\sigma_{2,\lambda_2}} = \frac{D^{\Sigma}_{\lambda_1} - \sigma_{1,\lambda_1}C_{1,eq}l}{D^{\Sigma}_{\lambda_2} - \alpha_1\sigma_{1,\lambda_1}C_{1,eq}l} = \frac{D^{\Sigma}_{\lambda_1} - D^{(1)}_{\lambda_1}}{D^{\Sigma}_{\lambda_2} - \alpha_1 D^{(1)}_{\lambda_1}} \; . \qquad (17)$$

Checking of the method by the model problem

A process of type (1) was studied. It was accepted that

$$A \rightleftharpoons I_1,\ K_1 = 10^{0.5}\exp[-10.00\ \text{kcal mol}^{-1}/(RT)];$$
$$A \rightleftharpoons I_2,\ K_2 = 10^{1.6}\exp[-20.00\ \text{kcal mol}^{-1}/(RT)]. \qquad (18)$$

The parameters of the real setup, the initial values of the temperature and pressure, and extinction coefficients of the intermediates for a series of the λ_m wavelengths (Table 1) were specified. A mixture of 5% methylenecyclopropane (MCP) with argon was chosen as a model system. For this mixture, the temperature dependence of the thermal capacity was calculated taking into account the published data.[9]

Table 1. Initial data for the solution of the model problem (18)

m	$\sigma_{1,\lambda_m}\cdot 10^{-5}$	$\sigma_{2,\lambda_m}\cdot 10^{-5}$	β_m
1	1	0	0.082
2	5	0.5	0.499
3	10	2	1.0
4	7.5	4	0.753
5	5	7	0.506
6	3	10	0.310
7	1.5	5	0.155
8	0.5	1	0.051

Note: m = 1—8 correspond to the λ_m wavelengths in the spectra of I_1 and I_2 at which the extinction coefficients (cm^2 mol^{-1}) have the values presented in the second and third columns in Table 1.

The direct problem was solved: a system of equations describing the process of the adiabatic compression of the gas accompanied by the chemical reactions in a free-piston setup. The problem was supplemented by the Bouguer—Lambert—Beer equations.[3] The calculation gave the curves of the temperature, pressure, and light absorption for several wavelengths under different conditions. The typical curves are presented in Fig. 1, *a*, *b*. The $Z_1 = Z_1[1/(RT_{max})]$ dependence was plotted at the λ_1 wavelength (see Table 1, m = 3) from the data presented in Table 2 and ΔQ_1 = 9.99 kcal mol^{-1} (the error of determination was 0.1%) and $\sigma_{1,\lambda_1}A_1 = 10^{6.50}$ were obtained. For the solution of the direct problem $A \rightleftharpoons I_1$ with the determined $\sigma_{1,\lambda_1}A_1$ and ΔQ_1 values, the time dependences of the light absorption are satisfactorily described in the whole temperature range. The β_m value was calculated from the light absorption at T_{max} = 707 K (see Table 1). Then, using ΔQ_1 and

Table 2. Results of the solution of the model problem (18)

p_{max} /atm	ε_{max}	$(\Delta J/J_0)_{\lambda_1}$ (%)	$(\Delta J/J_0)_{\lambda_2}$ (%)	$1000/T_{max}$ /K^{-1}
14.19	5.870	14.29	4.66	1.41
15.68	6.288	18.53	6.19	1.37
17.27	6.722	23.52	8.10	1.33
18.96	7.171	29.20	10.40	1.29
20.75	7.636	35.53	13.14	1.26
22.65	8.116	42.36	16.38	1.23
24.67	8.612	49.53	20.14	1.19
26.79	9.124	56.83	24.43	1.16
29.04	9.652	64.01	29.25	1.14
31.41	10.197	70.84	34.55	1.11
33.90	10.757	77.84	40.29	1.09
36.52	11.335	82.63	46.38	1.06

$\beta_m\sigma_{1,\lambda_1}A_1 = \sigma_{1,\lambda_m}A_1$, the light absorption caused by the first intermediate at the λ_m wavelengths (see Table 1) at T_{max} = 901 K was determined. The maximum difference between the total light absorption and the light absorption by the first intermediate was determined from Fig. 3. It is seen that this difference corresponds to the data in Table 1.

At T_{max} = 707 K, α_1 = 0.310 was calculated (the error of determination was 3.3%); at T_{max} = 942 K, we obtained α_2 = 0.204 (error 2.0%). It is noteworthy that the greater the contribution of the second intermediate to the total optical density, the less the error of determination of α_2. This is achieved at the highest temperature of T_{max}, at which the initial assumptions are still fulfilled (which was checked by the computer simulation).

Using the obtained α_1 and α_2 values, we calculated from Eqs. (9) and (10): $\sigma_{1,\lambda_1}A_1 = 10^{6.48}$, ΔQ_1 = 9.93 kcal mol^{-1} (the error of determination of ΔQ_1 was 0.7%) and $\sigma_{2,\lambda_2}A_2 = 10^{8.18}$, ΔQ_2 = 22.84 kcal mol^{-1} (determined from six points of the high-temperature region, the error for ΔQ_2 was 14.2%). Thus, the error of determination of α_1 of 3.3% resulted in the high error for ΔQ_2. Approximation (16) was too rough even at the lowest temperature of T_{max}. Let us estimate α_1 more exactly:

$$\frac{D^{\Sigma}_{\lambda_2}}{D^{\Sigma}_{\lambda_1}} = \frac{D^{(1)}_{\lambda_2} + D^{(2)}_{\lambda_2}}{D^{(1)}_{\lambda_1} + D^{(2)}_{\lambda_1}} = \frac{D^{(1)}_{\lambda_2}}{D^{(1)}_{\lambda_1}} + \frac{D^{(2)}_{\lambda_2}D^{(1)}_{\lambda_1} - D^{(1)}_{\lambda_2}D^{(2)}_{\lambda_1}}{D^{(1)}_{\lambda_1}(D^{(1)}_{\lambda_1} + D^{(2)}_{\lambda_1})} =$$

$$= \alpha_1 + \frac{D^{(2)}_{\lambda_2}(1-\alpha_1\alpha_2)}{D^{\Sigma}_{\lambda_1}},$$

from where

$$\alpha_1 = \frac{\alpha_2 D^{\Sigma}_{\lambda_2} + D^{(1)}_{\lambda_1} - D^{\Sigma}_{\lambda_1}}{\alpha_2 D^{(1)}_{\lambda_1}}. \qquad (19)$$

According to formula (19), at T_{max} = 707 K we obtain α_1 = 0.301 (the error of determination was 0.33%). When the refined α_1 value was used, $\sigma_{2,\lambda_2}A_2 = 10^{7.62}$ and ΔQ_2 = 20.15 kcal mol^{-1} (the error for ΔQ_2 was 0.7%) were determined from six points of the high-temperature region (Fig. 4).

Thus, in the solution of the model problem (see Eqs. (18)), taking into account the errors of the calculation of the model curves and determination of α_1 and α_2, the error of the method for calculating the heats of the formation of both intermediates can be estimated as 0.7%.

Let us estimate the error of determination of ΔQ_1 and ΔQ_2 from the experimental data. For this purpose, the error of the experimental measurements of the magnitudes in the calculation formulas should be taken into account in the solution of the model problem (where the exact result is known beforehand). The most important aspects of measurements, which are necessary for the calculation, are the following.

1. When the initial assumptions of the method are fulfilled, the experimentally detected time dependence of the pressure has the form of a curve symmetrical relative to t_0. It can be satisfactorily described by the Lorentzian dependence:

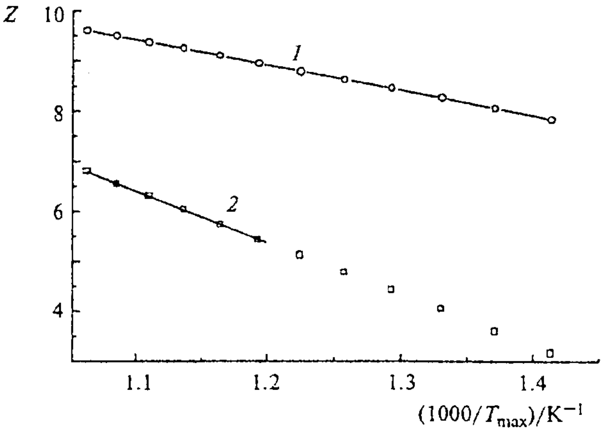

Fig. 4. Calculation of the model problem (18) in coordinates of Eqs. (11) and (12): *1*, I_1; *2*, I_2.

$$p = p_0 + \frac{2L}{\pi}\cdot\frac{\omega}{4(t-t_0)^2+\omega^2},$$

where p_0 is the initial pressure of the mixture (experimental value); L and ω are constant coefficients; and t is the independent variable (time).

The L, ω, and t_0 coefficients are selected automatically during approximations indicating errors. In addition, the moment of the maximum compression $t = t_0$ is determined. Then $p_{max} = p(t_0) = p_0 + 2L/(\pi\omega)$. The error of determination of Δp_{max} is determined, taking into account the ΔL and $\Delta\omega$ values obtained by the approximation.

2. The compression degree is calculated from the formula $\varepsilon_{max} = x_0/\delta$, where $x_0 \pm 0.05$ mm is the working length of the cylinder; $\delta \pm 0.02$ mm is the lengths of the indicator of the compression degree. In our study, the compression degree ranged from 8 to 18. Five measurements of the length of the indicator of the compression degree gave the average relative error of the measurement of the compression degree equal to 0.05% for this range.

3. The optical measurements gave the time dependence of the light absorption. This curve was smoothed by the formula $S_i = (Y_{i-1} + Y_i + Y_{i+1})/3$. When the smoothed curve is symmetrical, it is satisfactorily described by the Gaussian dependence:

$$\frac{\Delta J}{J_0} = L\exp\left[-\frac{(t-t_0)^2}{2\omega^2}\right],$$

where L and ω are constants and t is time.

Then $\left.\frac{\Delta J}{J_0}\right|_{max} = \frac{\Delta J}{J_0}(t_0) = L$. It was found that noises from the light source are ±(1.5—2.0)%. However, since the number of the experimental points in one experi-

Table 3. Contribution of the errors of measurements of the experimental values to the total error in the calculation of the heats

Measurement error (%)	Determination error /kcal mol^{-1} (%)	
	ΔQ_1	ΔQ_2
$\delta(p_{max})/p_{max} = \pm 0.2$	0.025 (0.25)	0.053 (0.27)
$\delta(\varepsilon_{max})/\varepsilon_{max} = \pm 0.05^a$	0.008 (0.08)	0.008 (0.04)
$\delta\left(\frac{\Delta J}{J_o}\Big\vert_{t=0}\right) = \pm 0.5$	0.265 (2.67)^b	0.610 (3.06)
$\delta(x_A)/x_A = \pm 5.3$	0.004 (0.04)	0.020 (0.10)

[a] The mean value in the studied interval of compression degrees.

[b] The error given previously[6] was refined.

ment was ~100, the error of the value of the L amplitude calculated from the approximating curve for the series of experiments at 237.5 nm was 0.5%.

The contribution of the errors of the experimental measurements to the total error in the calculation of ΔQ_i was estimated at the values $\alpha_1 = 0.3$ and $\alpha_2 = 0.2$ specified beforehand. For this purpose, the sensitivity of the heats values to errors in experimental values was determined in turn. The contributions of the errors of the experimental measurements of the parameters to the total error in the calculation of the heats are presented in Table 3.

Taking into account the above determined error of the method for the model problem (18), the total error was 3.8% for ΔQ_1 and 4.2% for ΔQ_2.

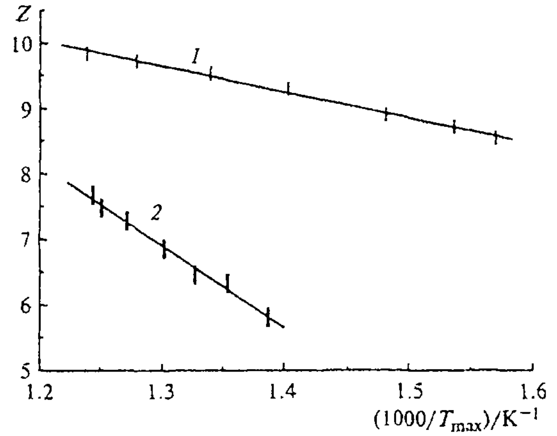

Fig. 5. Processing of experimental data in coordinates of Eqs. (11) and (12): *1*, TMM; *2*, but-1-ene-2,4-diyl.

Table 4. Data for calculation of the heats of the formation of TMM

p_{max} /atm	ε_{max}	$(\Delta J/J_0)_{\lambda_1}$ (%)	$1000/T_{max}$ /K^{-1}
18.1	8.44	14.5	1.57
19.8	9.04	20.0	1.54
23.0	10.13	26.0	1.48
28.7	11.99	41.0	1.40
34.8	13.87	53.6	1.34
42.1	16.03	65.8	1.28
48.0	17.68	73.4	1.24

Application of the method to the specific experiment

The formation of intermediates during the adiabatic compression of a mixture with the following composition was studied: MCP (2 vol.%) + CO_2 (40 vol.%) + Ar (58 vol.%). The light absorption was detected in the wavelength range from 220 to 260 nm with an increment of 5 nm (in the 235—250 nm range, with an increment of 2.5 nm) at T_{max} = 640, 710, and 800 K. Under these conditions, λ_1 = 237.5 nm. It has been previously shown[5] that the light absorption at this wavelength is due to TMM (I_1). The second intermediate I_2 is observed at T_{max} = 710 K (according to the published data,[5] this is the but-1-ene-2,4-diyl biradical, $CH_2{=}^{\cdot}C{-}CH_2{-}^{\cdot}CH_2$). Its presence was determined from the appearance of a "shoulder" in the spectrum (see Fig. 2, curve *2*). Then the kinetic curves of the light absorption at λ_1 = 237.5 nm (see Fig. 1, *a*) and at the wavelengths in the 245—250 nm range corresponding to this "shoulder" were compared. A substantial difference between the time dependences of the light absorption was observed. The kinetic curve of the light absorption at λ = 247.5 nm is presented in Fig. 1, *b* as an example. It can be seen that at approximately equal amplitudes of the signal, the half-widths of the curves differ noticeably. This comparison is reasonable only for close values of the light absorption in maxima of the experimental curves. Thus, the appearance of the second intermediate during the adiabatic compression of the mixture considered was established from two independent properties.

To determine ΔQ_1, a series of experiments were performed at λ_1 = 237.5 nm and different ε_{max} values. The measured and calculated values necessary for the calculation are presented in Table 4. Typical experimental time dependences of the pressure and light absorption are presented in Fig. 1, *a*. The results of processing the data in Table 4 using the $Z_1 = Z_1[1/(RT_{max})]$ dependence (the procedure for processing has been described previously[6]) are illustrated in Fig. 5 (curve *1*). The $(1/T_{max})$—Z_1 dependence is established to be satisfactorily described by a straight line in the whole temperature interval rather than at the 640—710 K intersection only. The determined value of the heats of the reaction was 7.85±0.25 kcal mol^{-1} (the error of determination of ΔQ_1 was 3.2%)*. The relative extinction coefficients β_m were calculated from the absorption spectrum of I_1 detected at T_{max} = 640 K. The results of the calculation of $(\Delta J/J_0)^{(1)}_{\lambda_m}$ for T_{max} = 710 K (curve *3*)

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* The error was estimated by the Peters formula.[10]

Table 5. Data for calculation of the heats of the formation of but-1-ene-2,4-diyl

$p_{\max}$ /atm	$\varepsilon_{\max}$	$(\Delta J/J_0)_{\lambda_1}$ (%)	$(\Delta J/J_0)_{\lambda_2}$ (%)	$1000/T_{\max}$ /K^{-1}
30.3	12.29	44.2	14.5	1.39
33.5	13.27	51.2	18.3	1.35
36.5	14.17	57.4	21.5	1.33
39.5	15.04	63.1	25.8	1.30
43.5	16.19	70.0	31.9	1.27
46.8	17.11	74.9	36.5	1.25
47.9	17.49	76.5	39.4	1.24

and the experimental $(\Delta J/J_0)_{\lambda_m}{}^{\Sigma}$ values (curve *2*) are presented in Fig. 2. It is seen that the maximum difference between the amplitudes of the total (experimental) light absorption and that calculated for I_1 at the same temperature falls on 247.5 nm. As mentioned previously, this is λ_2.

After the determination of λ_2 at this wavelength, the time dependence of the pressure and light absorption were experimentally studied at $T_{\max}$ within the range from 640 to 805 K. Using Eq. (16), we obtained α_1 = 0.24. Before the determination of α_2 by formula (17), it should be mentioned that, in the general case (less favorable), the differences between close values are in both the numerator and denominator in Eq. (17). The error can exceed 100%. It is evident that $1 > \alpha_2 \geq 0$. However, it is seen in Fig. 2 that beginning from $\lambda <$ 240 nm, curves *2* and *3* coincide within the experimental error. This means that I_2 does not contribute to the light absorption at 237.5 nm. The absence of this contribution can be explained only by the fact that $\sigma_{2,\lambda_1} \ll \sigma_{1,\lambda_1}$. Therefore, we can accept that $\alpha_2 \approx 0$.

In this case, $(\Delta J/J_0)^{\Sigma}{}_{237.5} \approx (\Delta J/J_0)^{(1)}{}_{237.5}$ and $D^{\Sigma}{}_{237.5} \approx D^{(1)}{}_{237.5}$. These values can be calculated for any temperature in the range studied using the previously obtained ΔQ_1 and $\sigma_{1,\lambda_1}A_1$ values. Therefore, studying the light absorption at λ_1 and λ_2, there is no need to carry out experiments under the same conditions. Using the data in Table 5, we obtained* $\Delta Q_2 = 25.0\pm1.2$ kcal mol^{-1} from Eq. (12) (see Fig. 5, curve *2*). Note that the ΔQ_1 value calculated from Eq. (11) is equal to 7.71 ± 0.29 kcal mol^{-1}. After the determination of ΔQ_1 and ΔQ_2, using the published[11] value of the enthalpy of the formation of MCP, it is not difficult to obtain the enthalpies of the formation of singlet TMM (55.7 ± 0.65 kcal mol^{-1}) and but-1-ene-2,4-diyl (73.0 ± 1.6 kcal mol^{-1}).

It should be mentioned in conclusion that both the necessary conditions of applicability of the method are fulfilled in this case. First, the chemical equilibrium is achieved at the moment of maximum compression t_0 due to specific features of the adiabatic compression. Second, only the reverse reaction of the cycle closing is possible[12] at maximum temperatures within the 640 K $\leq T_{\max} \leq$ 805 K range for singlet TMM: no transformation of the starting substance into stable products (through but-1-ene-2,4-diyl) was observed by GLC.

Thus, the new method for the determination of heats of thermal gas-phase reactions of the formation of intermediate species in terms of the adiabatic compression method was extended for the processes with the formation of two intermediates with overlapping spectra.

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References

1. N. N. Buravtsev, Yu. A. Kolbanovskii, and A. A. Ovsyannikov, *Mendeleev Commun.*, 1994, 48.
2. N. N. Buravtsev, Yu. A. Kolbanovskii, and A. A. Ovsyannikov, *Izv. Akad. Nauk, Ser. Khim.*, 1995, 2048 [*Russ. Chem. Bull.*, 1995, **44**, 1967 (Engl. Transl.)].
3. N. N. Buravtsev, L. S. German, A. S. Grigor'ev, Yu. A. Kolbanovskii, A. A. Ovsyannikov, and A. Yu. Volkonskii, *Mendeleev Commun.*, 1993, 133.
4. N. N. Buravtsev, A. S. Grigor'ev, Yu. A. Kolbanovskii, and A. A. Ovsyannikov, *Dokl. Akad. Nauk*, 1994, **339**, 616 [*Dokl. Phys. Chem.*, 1994 (Engl. Transl.)].
5. I. V. Bilera, N. N. Buravtsev, Yu. A. Kolbanovskii, and A. A. Ovsyannikov, *Dokl. Akad. Nauk*, 1996, **348**, 620 [*Dokl. Phys. Chem.*, 1996, **348**, 133 (Engl. Transl.)].
6. N. N. Buravtsev, Yu. A. Kolbanovskii, and A. A. Ovsyannikov, *Izv. Akad. Nauk, Ser. Khim.*, 1996, 64 [*Russ. Chem. Bull.*, 1996, **45**, 56 (Engl. Transl.)].
7. Yu. A. Kolbanovskii, V. S. Shchipachev, N. Ya. Chernyak, A. S. Chernysheva, and A. S. Grigor'ev, *Impul'snoe szhatie gazov v khimii i tekhnologii* [*Pulse Compression of Gases in Chemistry and Technology*], Nauka, Moscow, 1982 (in Russian).
8. Yu. A. Kolbanovskii, *Usp. Khim.*, 1989, **58**, 1800 [*Russ. Chem. Rev.*, 1989, **58** (Engl. Transl.)].
9. D. R. Stull, E. F. Westrum, Jr., and G. C. Sinke, *The Chemical Thermodymamics of Organic Compounds*, J. Wiley and Sons, New York, 1969.
10. G. L. Squires, *Practical Physics*, McGraw-Hill, London, 1968.
11. J. B. Pedley, R. D. Naylor, and S. P. Kirby, in *Thermochemical Data of Organic Compounds*, Chapman and Hall, London—New York, 1986, 89.
12. R. J. Crawford and D. M. Cameron, *J. Am. Chem. Soc.*, 1966, **118**, 2589.

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* The refined value $\alpha_1 = 0.23$ was used instead of $\alpha_1 = 0.24$ presented above.