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Reaction Kinetics of the Redox Decomposition of Hydroxymercurated Propylene in Aqueous Solution Followed by Time-Sequential NMR Spectroscopy

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The redox decomposition process of hydroxymercurated propylene in aqueous solution yielding acetone has been followed by time-sequential NMR spectroscopy *in situ*. No reaction intermediates and reaction products other than acetone were observed. Stoichiometric relationship holds between the reactant and the product during the reaction, which was verified by NMR spectra. The reaction rate was confirmed to be of first order with respect to mercurial. Although the rate was accelerated at higher acidity in solution, a similar rate enhancement took place by addition of neutral salts. At a certain ionic strength, no close linear correlation between the apparent rate constants and proton concentration was observed. In contrast, excellent linear dependence was obtained by the thermodynamic activities of the added electrolytes including acid. Since the apparent rate constant was independent of the concentration of free mercuric ion, a monomolecular mechanism is proposed. Taking into account the rate dependence upon added electrolytes, the redox decomposition of the hydroxymercurated olefins to give carbonyl compounds seems to proceed only when an aquo ligand is removed from the carbon-bonded mercuric ion.

Olefin oxidation by metal ions in aqueous solution has long been investigated from the industrial, synthetic, and mechanistic viewpoints, with a good deal of knowledge compiled for Pd(II)[1] and Tl(III)[2] as well as for Hg(II).[3–5] Similarities and contrasts were pointed out by Henry between Pd(II) and Tl(III) in olefin oxidation.[6] Although common reaction products, *i.e.*, saturated carbonyl compounds, are obtainable,[5] little attention has been paid to Hg(II) oxidation. In order to elucidate the catalytic oxidation of olefins with metal ions, comparison from the mechanistic viewpoint seems to be indispensable between Pd(II), Tl(III), and Hg(II) oxidation. The reaction schemes of the σ-complex formation *via* π-complex intermediates are commonly postulated for these metal ions toward olefins. In the case of Hg(II), σ-complex is considered to be formed *via* mercurinium ion, a π-complex intermediate.[7] The redox decomposition of the σ-complexes is known to proceed fast for both Pd(II) and Tl(III) oxidation, but slowly for Hg(II) oxidation, which is ascribed to the stability of β-hydroxyalkylmercury(II) complexes. Thus information concerning the redox decomposition step of σ-complexes can only be afforded by studying Hg(II) oxidation.

The first order kinetics with respect to free mercuric ion was confirmed for the formation of unsaturated carbonyl compounds.[3] However, proton dependence on the rates of redox decomposition has never been investigated in spite of the following facts. (1) The rate of hydroxymercuration of olefins[8] is independent of proton concentration. (2) The rate of deoxymercuration yielding original olefins[7] is dependent on proton concentration, since proton is incorporated in the pre-equilibrium step of deoxymercuration. In the present work, kinetics on both proton and free mercuric ion as well as neutral salt effects were studied in order to elucidate the reaction mechanism of the redox decomposition of hydroxymercurated olefins yielding saturated carbonyl compounds. The time-sequential NMR spectroscopy was adopted to monitor the reaction, since it affords the possibility for detecting reaction intermediates, if any.

Experimental

Materials. All the reagents were of G.R. grade, prepared by Kojima Kagaku Co., Ltd. (Tokyo), and were used without further purification. Absence of impurities was confirmed by gas chromatography using a β,β'-dioxypropionitrile column for each gaseous olefin prepared by Takachiho Kagaku Kogyo Co., Ltd. (Tokyo). Mercuric solutions were prepared by dissolving mercuric nitrate into concentrated nitric acid, which was diluted with ion-exchanged water up to a given concentration. The concentration of mercuric ion was determined by titration with potassium thiocyanate.

Procedure. Propylene was introduced from the cylinder for 2 min at room temperature into 10 m*l* of the aqueous solution consisting of 6.5 g (20 mmol) of mercuric nitrate and 0.69 g (11 mmol) of nitric acid with or without additional electrolytes. The concentration dependence of the free mercuric ion was studied for the series of solutions consisting of a certain amount of hydroxymercurated propylene and of various amounts of free mercuric ion. The concentration of hydroxymercurated propylene, which is stable at room temperature, was determined from the NMR peak intensity by comparing it with that of the external tetramethylsilane reference.

The time-sequential NMR spectra were obtained at a given temperature with a JEOL C-60 NMR spectrometer constructed by Japan Electron Optics Laboratory Co. Ltd. The reaction temperature was regulated by blowing cooled nitrogen gas and determined by the relative chemical shifts of 1,3-propanediol. The reaction was thus followed by NMR spectroscopy *in situ*.

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[1] a) E. W. Stern, "Catalysis Reviews," Vol. I. (1968), p. 74; b) A. Aguilo, "*Adv. Organometal. Chem.*," Vol. V. (1967), p. 321.

[2] P. M. Henry, *J. Amer. Chem. Soc.*, **87**, 990, 4423 (1965); **88** 1597 (1966).

[3] B. C. Fielding and H. Roberts, *J. Chem. Soc., A*, **1966**, 1627.

[4] J. C. Strini and J. Metzer, *Bull. Soc. Chem. Fr.*, 3145, 3150 (1966).

[5] Y. Saito and M. Matsuo, *J. Organometal. Chem.*, **10**, 524 (1967).

[6] P. M. Henry, *Adv. Chem. Ser.*, **52**, 126 (1968).

[7] W. Kitching, *Organometal. Chem. Rev.*, **3**, 61 (1968) and references therein.

[8] J. Halpern and H. B. Tinker, *J. Amer. Chem. Soc.*, **89**, 6427 (1967).

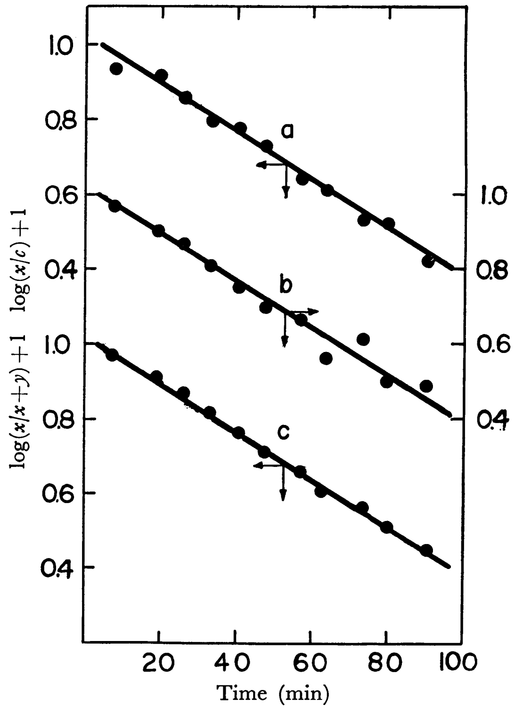

Fig. 1. Reaction kinetics represented by the following three equations.
a. $\ln[x/c] = -kt$
b. $\ln[1-(y/c)] = -k't$
c. $\ln[x/(x+y)] = -k''t$
where x and c are the concentrations of hydroxymercurated propylene at time t and $t=0$, respectively, and y is that of acetone at time t.

The first order rate equation for the redox decomposition with respect to hydroxymercurated olefin was ascertained previously⁵⁾ by comparing three kinds of parallel straight lines, obtained from the peak decrease of the reactant mercurial *versus* the external reference, from the peak increase of the product ketone *versus* the reference, and from mercurial *versus* ketone without intermediary of tetramethylsilane. A typical example of the analysis is shown in Fig. 1.

Calculation of thermodynamic activities of electrolytes. With regard to the estimation of thermodynamic activities, the square root of ionic strength is not a good measure of concentrations higher than *ca.* 0.1 molality in aqueous solution. However, it was verified at elevated temperatures that the logarithms of the activity coefficient of hydrogen chloride in aqueous solution mixed with sodium chloride or of hydrogen bromide mixed with potassium bromide varied linearly with concentration up to about 3 molality.9)

It is assumed, therefore, that a linear relationship holds between the logarithm of the activity coefficient of a certain electrolyte in aqueous solution and the concentration of the added electrolyte in the present solutions as well. Since the activity coefficients of electrolytes such as nitric acid, lithium nitrate, sodium nitrate, potassium nitrate, and sodium perchlorate in aqueous solution as a single component are all available up to highly concentrated regions,10) the values of the activity coefficients of each electrolyte in the mixed aqueous solution can thus be calculated on the basis of the above-mentioned assumption.

Results

Dependence of Reaction Rates on Acid and Salt Concentration. Although the rate of the redox decomposition of hydroxymercurated propylene yielding acetone5) was determined to be first order with respect to the concentration of hydroxymercurated propylene, no kinetic investigation concerning the concentration of either proton or free mercuric ion has been carried out. At a certain ionic strength, *i.e.*, $\mu=9.49$, regulated by adding either lithium nitrate, sodium nitrate, or potassium nitrate, the concentration of nitric acid increased and monotonous enhancement of rate constants was obtained at 45.6°C as shown in Fig. 2.

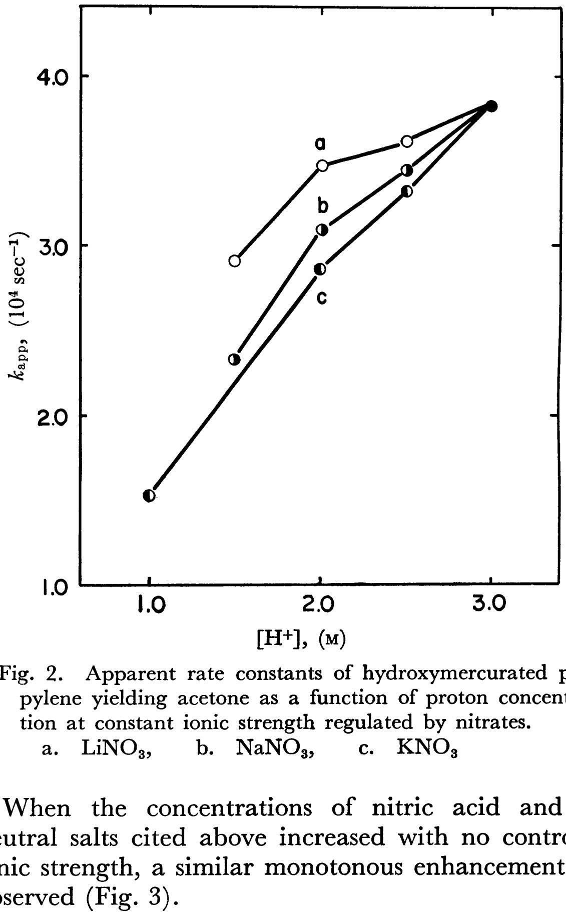

Fig. 2. Apparent rate constants of hydroxymercurated propylene yielding acetone as a function of proton concentration at constant ionic strength regulated by nitrates.
a. $LiNO_3$, b. $NaNO_3$, c. KNO_3

When the concentrations of nitric acid and the neutral salts cited above increased with no control in ionic strength, a similar monotonous enhancement was observed (Fig. 3).

Dependence of the Reaction Rates on Acid and Salt Activity. Excellent linear relationship between the rate constants and the estimated thermodynamic activities of added electrolytes were found for nitric acid, lithium nitrate, sodium nitrate, potassium nitrate, and sodium perchlorate (Fig. 4).

A better linearity is found in Fig. 4 than in Fig. 3. The apparent rate constants are, therefore, not correlated to the concentrations but to the activities of added electrolytes. All the results are summarized in Table 1.

The rate equation to yield acetone from hydroxymercurated propylene, given previously as

$$v = k_{app}\,[\text{mercurial}], \tag{1}$$

should be expressed as

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9) M. L. Lietzke, *J. Phys. Chem.*, **69**, 2395 (1965).

10) R. Parsons, Handbook of Electrochemical Constants, Butterworths, New York (1959), p. 20.

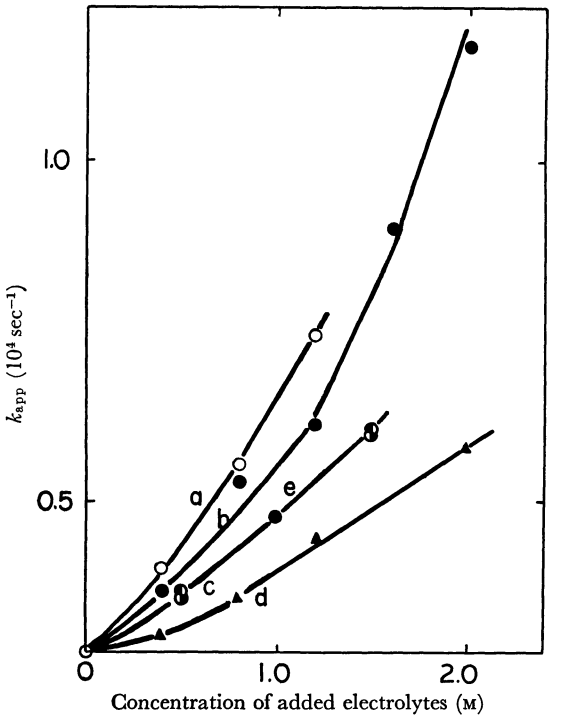

Fig. 3. Plots of apparent rate constants of hydroxymercurated propylene yielding acetone as a function of the concentrations of added electrolytes.
a. HNO_3, ○ b. $LiNO_3$, ● c. $NaNO_3$, ◑
d. KNO_3, △ e. $NaClO_4$, ◐

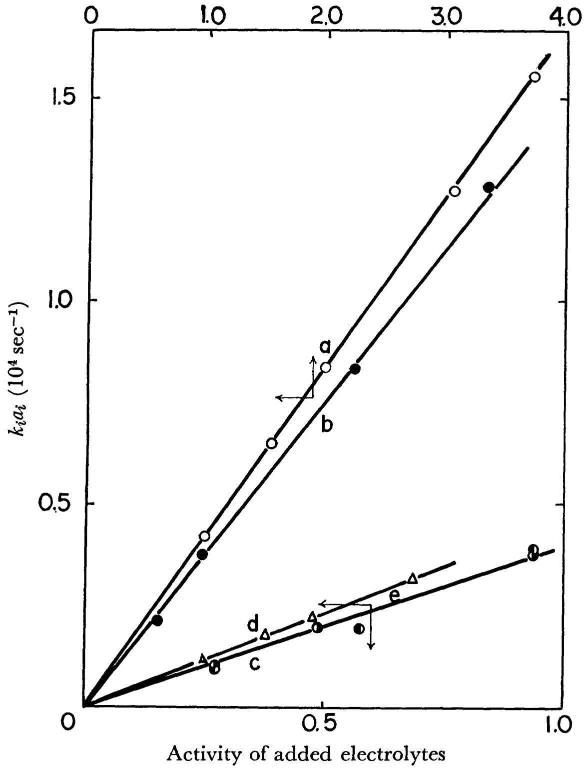

Fig. 4. Correlation of apparent rate constants of hydroxymercurated propylene yielding acetone with the thermodynamic activities of added electrolytes.
a. HNO_3, ○ b. $LiNO_3$, ● c. $NaNO_3$, ◑
d. KNO_3, △ e. $NaClO_4$, ◑

Table 1. APPARENT RATE CONSTANTS OF THE REDOX DECOMPOSITION OF HYDROXYMERCURATED PROPYLENE IN CORRELATION TO THE CONCENTRATION AND THE ACTIVITY OF ADDED ELECTROLYTES

Added acid Concentration (M)	Added acid activity (M)	Added salts Concentration (M)	Added salts activity (M)	k_{app} (sec^{-1})
HNO_3		$LiNO_3$		
1.60	1.67	0.04	0.48	9.8×10^{-3}
	1.78	0.80	1.00	13.4
	2.17	1.60	2.38	20.3
	2.58	2.00	3.32	26.0
HNO_3		$NaNO_3$		
1.60	1.69	0.50	0.29	10.3
	1.87	1.00	0.51	12.3
	2.13	1.50	0.91	15.2
HNO_3		KNO_3		
1.60	1.67	0.40	0.27	8.3
	1.87	0.80	0.39	9.2
	1.98	1.20	0.49	10.7
	2.58	2.00	0.69	14.2
HNO_3		$NaClO_4$		
1.60	1.69	0.50	0.30	10.8
	1.87	1.00	0.61	12.0
	2.13	1.50	0.93	15.4
HNO_3				
1.20	1.08			5.2
1.60	1.52			7.3
2.00	2.16			9.3
2.40	2.96			12.1
2.80	3.65			16.3

$$v = (k_0 a_0 + k_i a_i)\ [\text{mercurial}], \tag{2}$$

where k_0 and a_0 are the rate constant and the thermodynamic activity of HNO_3, and k_i and a_i are the corresponding quantities of added neutral salts. The rate constant k_0 for HNO_3 was obtained as 4.5 g/sec·mol and k_i for $LiNO_3$, $NaNO_3$, KNO_3, and $NaClO_4$ as 4.0, 4.8, 5.2, and 4.8 g/sec·mol, respectively. The effect of nitric acid on rate enhancement was thus eventually equal to that of neutral salts.

Dependence of Reaction Rates on Free Mercuric Ion Concentration. The apparent rate constants given in Eq. (1) were independent of the concentrations of free mercuric ion as shown in Fig. 5. The first order kinetics with respect to free mercuric ion was established for acrolein formation from hydroxymercurated propylene.[3] The reaction kinetics of acetone formation from the same reactant is in contrast to that of acrolein formation. Although both are redox decomposition products of hydroxymercurated propylene, it is to be noted that the change of oxidation state of the former is four, while that for the latter is two.

Time-sequential NMR Spectra for Monitoring the Reaction. No reaction intermediates or products other than acetone were recognized and no chemical shifts of the mercurial signals during the reaction process were observed in the time-sequential NMR spectra. Stoichiometric relationships between the reactant mercurial and the product acetone were confirmed from peak heights.

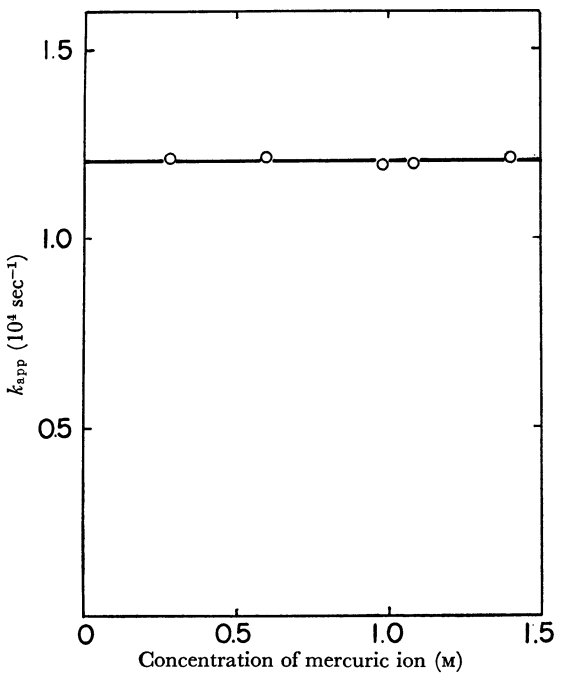

Fig. 5. Apparent rate constants of hydroxymercurated propylene yielding acetone as a function of the concentration of free mercury(II) ions.

Discussion

Influence of the Activities of Added Electrolytes on Reaction Rates. It should be noted that the concentration level of the electrolytes adopted in the present work is far higher than the values ordinarily used for the reactions in aqueous solutions[11] due to the need of NMR observation. This is why considerations were made not only on concentrations but also on activities, and the activity coefficients of electrolytes were calculated by the above-mentioned method.

As far as a reaction of first order with respect to a reactant A (including a pre-equilibrium step $\mathrm{A}+\mathrm{B} \rightleftharpoons \mathrm{C} \rightarrow \mathrm{X}+\mathrm{Y}$) is concerned, the rate equation is given by

$$v = k_{\mathrm{app}}[\mathrm{A}] = k_0[\mathrm{C}], \tag{3}$$

where k_{app} and k_0 are apparent and true rate constants, respectively. Since the equilibrium constant K is given as the ratio of activities,

$$K = \frac{a_{\mathrm{C}}}{a_{\mathrm{A}}a_{\mathrm{B}}} = \frac{[\mathrm{C}]}{[\mathrm{A}][\mathrm{B}]}\frac{\gamma_{\mathrm{C}}}{\gamma_{\mathrm{A}}\gamma_{\mathrm{B}}} \tag{4}$$

the following rate equation is derived.

$$v = k_0K\frac{\gamma_{\mathrm{A}}\gamma_{\mathrm{B}}}{\gamma_{\mathrm{C}}}[\mathrm{A}][\mathrm{B}] = ka_{\mathrm{B}}[\mathrm{A}] \tag{5}$$

where $k = k_0K\gamma_{\mathrm{A}}/\gamma_{\mathrm{C}}$ is used for brevity. By comparing Eqs. (3) and (5), a linear relationship between k_{app} and a_{B} would be anticipated for the runs of different high concentration levels of B, as far as the participation of the substance B to the reaction is expected at the pre-equilibrium step.

With regard to the redox decomposition reaction of hydroxymercurated propylene followed by NMR spectroscopy *in situ*, it has been ascertained in Fig. 3 and Fig. 4 that a linear correlation with the reaction rates is not obtained for the concentrations but for the activities of the added electrolytes. This would suggest the participation of these added electrolytes to the reaction at a pre-equilibrium step, since the electrolytes can reduce water activities of the solutions, with an aquo ligand replaced from the mercurial to the electrolyte. In other words, the step of an aquo ligand removal from the carbon-bonded mercuric ion would be assumed prior to its redox decomposition as follows.

$$\mathrm{CH_3CH(OH)CH_2Hg^+(OH_2) + MX \rightleftharpoons CH_3CH(OH)CH_2Hg^+ + MX(OH_2)} \tag{6}$$

$$\mathrm{CH_3CH(OH)CH_2Hg^+ \longrightarrow CH_3COCH_3 + Hg(0) + H^+} \tag{7}$$

Although water activities in the solutions can be calculated by use of the Gibbs-Duhem equation, no additional data processing was made, as undesirable decrease in reliability might take place in high concentration region.

It is known that the rate of ethylene oxidation by Tl(III) in aqueous solution is of first order in the concentration of both Tl(III) and ethylene.[2] The rate is considerably accelerated by increasing salt concentration, the effect being related also to changes in the activity of water. It was presumed that more complexing between the metal ions and olefins would occur at lower water activity,[12] since the lower the activity of water in the solution, the more vacant the ligand sites for the metal ions.

A similar acceleration with the increase of the ionic strength of the solution is also recognized in aromatic mercuration.[13]

No Rate Dependence on Free Mercuric Ion. First order kinetics with respect to the concentrations of both the mercurial and the free mercuric ion were reported for acrolein formation from hydroxymercurated propylene in similar acidic aqueous media.[3] As for acrolein formation, the four equivalent oxidation is necessary in total, whereas acetone is made by two equivalent oxidation. It seems, therefore, reasonable that zero order dependence on the free mercuric ion was found in the present reaction. Moreover, lack of incorporation of free mercuric ion in either pre-equilibrium steps or the rate-determining process for this two-equivalent oxidation reaction would suggest a monomolecular mechanism in which two-electron transfer takes place. It does not necessarily mean that metallic mercury is found in the reaction products, because the following disproportionation reaction is fast and the equilibrium is much favored to $\mathrm{Hg^{2+}}$ side.[14]

$$\mathrm{Hg(0) + Hg^{2+} \rightleftharpoons Hg_2{}^{2+}} \tag{8}$$

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[11] S. Glasstone, K. J. Laidler, and H. Eyring, "The Theory of Rate Processes", McGraw-Hill, New York (1941), p. 400.

[12] F. Basolo and R. G. Pearson, "Mechanism of Inorganic Reactions," 2nd ed., John Wiley and Sons, New York, (1967) p. 598.

[13] C. Perrin and F. H. Westheimer, *J. Amer. Chem. Soc.*, **85**, 2773 (1963).

[14] F. A. Cotton and G. Wilkinson, "Avanced Inorganic Chemistry," Intsci. Publ., New York, (1962) p.481.

Reaction Process Followed by Time-sequential NMR Spectroscopy. Generally speaking, chemical species prevailing in spectroscopy are not necessarily prevailing kinetically for reaction processes. As for spectroscopic approach to reaction analysis, monitoring the reaction process *in situ* is important for this reason. The time-sequential NMR spectroscopy is advantageous not only in qualitative discrimination or quantitative identification but also in molecular characterization of chemical species concerned, especially for reaction intermediates, if they exist above the detection level of high resolution NMR spectroscopy.

In the present reaction the concentration of the reaction intermediate of the successive type, $R \rightarrow I \rightarrow P$, was concluded to be sufficiently low, since no signals other than the reactant's and product's were found in each of the time-sequential spectra. Moreover, coincidence was recognized between the rate constants obtained from the reactant decrease and the product increase independently for the total period of the reaction. The contribution of reaction intermediates of the pre-equilibrium type, $R \rightleftharpoons I \rightarrow P$, would also be sufficiently small, since no change in chemical shifts during the reaction was observed.

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