Kinetic Study for Reactions of Nitrate Radical ($NO_3\cdot$) with Alcohols in Solutions

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The rate constants for the reaction of nitrate radical ($NO_3\cdot$) with alcohols have been determined by flash photolysis method in aqueous and nonaqueous solutions. The reactivity of $NO_3\cdot$ in acetonitrile was higher than that in aqueous solution, suggesting that hydrogen bonds between solvent and $NO_3\cdot$ or alcohols decrease the reaction rate. From the deuterium-isotope effect, the main reaction path was confirmed to be hydrogen atom abstraction from the carbon atom bonded with the OH group. For 2-methyl-2-propanol, the hydrogen atom abstraction from the OH group was presumed. These reaction paths were confirmed, since the reaction rate constants decreased with an increase in the corresponding bond-dissociation energies. From strong dependency of the rate constants upon the ionization energies of alcohols, the polar transition states of the reactions were suggested.

By photolysis of $(NH_4)_2[Ce(NO_3)_6]$ in the presence of alcohols, the intermediate radicals produced by the loss of the hydrogen atom from alcohols were observed by the low temperature ESR measurements and spin trapping technique.[1–3] As the initial step, it has been presumed that the electron transfer from alcohols to cerium(IV) ion occurs producing the radical cations of alcohols (Reaction 1), which undergo deprotonation forming the neutral radicals of alcohols (Reaction 2).[1–3]

$$\mathrm{R'R''CHOH} + \mathrm{Ce^{4+}} \xrightarrow{h\nu} \mathrm{R'R''CHOH^{+\cdot}} + \mathrm{Ce^{3+}} \quad (1)$$

$$\mathrm{R'R''CHOH^{+\cdot}} \longrightarrow \mathrm{R'R''C^{\cdot}OH} + \mathrm{H^+} \quad (2)$$

On the other hand, it was also reported by flash photolysis method that the nitrate radical ($NO_3\cdot$) was efficiently produced from $(NH_4)_2[Ce(NO_3)_6]$ in aqueous solution[4,5] and in nonaqueous solution.[6,7] For a few alcohols, the rate constants for the reaction with $NO_3\cdot$ in aqueous solution were determined by using the flash photolysis[8] and pulse radiolysis method.[9] The high reactivities of $NO_3\cdot$ with alcohols suggest that different reactions from Reactions 1 and 2 are responsible to the photooxidation of alcohols by $(NH_4)_2[Ce(NO_3)_6]$.

Since $NO_3\cdot$ also plays an important role in air pollution, many kinetic studies in gas phase have been reported.[10,11] By comparing the rate constants in gas phase with the corresponding ones in solutions, considerable differences attributable to the medium effect were found for the reactions with aldehydes in our previous paper.[12] In this study, we report the rate constants for the reactions of $NO_3\cdot$ with various alcohols in acetonitrile and in aqueous solution by using flash photolysis technique. In order to reveal the reaction paths, the deuterium-isotope effects on the reaction rates were investigated. The correlation of the observed rate constants with bond-dissociation energies also afforded information about the reaction mechanisms. The polar nature of the transition state for the reaction was also revealed.

Experimental

$K_2[Ce(NO_3)_6]$, which was used as a radical source, was prepared from the ammonium salt by the action of KOH. Alcohols were purified by distillation before use. Commercially available deuterium derivatives (Merck Co. INC.) were used as received; deuterium degrees for both CH_3OD and CD_3OD are >99%. Distilled acetonitrile (over P_2O_5 under N_2) and distilled water were used as solvents.

The xenon flash photolysis apparatus was of a standard design with two xenon flash-lamps (Xenon Corp. N-815C);[13,14] the half-duration was ca. 10 μs and input energy was ca. 100 J. By using the light filters, $K_2[Ce(NO_3)_6]$ was flash-photodecomposed with the light between 310 and 450 nm. The temperature of the reaction was controlled by dipping the flash cell (1 dm of optical lenght and 0.1 dm of diameter) in a cooled methanol bath or water bath. For the measurements of Arrhenius parameters, temperature was varied from −40 to 20 °C. Within this temperature range, spontaneous reaction between the radical source and alcohols was not observed in the dark. Above 50 °C, bleaching of yellow color of the radical source was observed on the addition of benzenemethanol (benzyl alcohol) as reported in the literature.[15]

Results and Discussion

Figure 1 shows a transient absorption spectrum appeared by the flash photolysis of $K_2[Ce(NO_3)_6]$ in acetonitrile. The absorption bands with vibronic structure (peak at 635 nm) are attributed to the absorption bands of $NO_3\cdot$ in acetonitrile, indicating that photodissociation Reaction 3 occurs efficiently even in acetonitrile.[6–9]

$$\mathrm{K_2[Ce^{IV}(NO_3)_6]} \underset{k_b}{\overset{h\nu}{\rightleftharpoons}} \mathrm{NO_3^{\cdot}} + \mathrm{K_2[Ce^{III}(NO_3)_5]} \quad (3)$$

Insert of Fig. 1 shows the first-order plots for the decay of $NO_3\cdot$ in the presence of alcohols. In the absence of alcohol, the decay of $NO_3\cdot$ was attributed to the back process of Reaction 3. The half-life of $NO_3\cdot$ in the absence of alcohols was ca. 1000 μs which is long enough to follow decay kinetics of $NO_3\cdot$ by our flash photolysis apparatus with half-duration of flash lamp of 10 μs even in the presence of excess of alcohols. In the presence of alcohol, a sufficiently linear line was obtained for each concentration. The slope yields pseudeo first-order rate constant ($k_{\text{first-order}}$). The decay rate increases with the concentration of additive. Since the concentration of $NO_3^{\cdot}$ produced by each flash exposure was evaluated less than ca. 1×10^{-6} mol dm^{-3} by assuming the extinction coefficient to be ca. 1000 dm^3 mol^{-1} cm^{-1} at 635 nm in acetonitrile,[3,4,16] the addition of alcohols higher than ca. 1×10^{-5} mol dm^{-3} is enough to establish pseudo first-order kinetics.

Figure 2 shows the pseudo first-order plots for various alcohols. The linear lines are obtained; from the slopes the second-order rate constants, which are referred to as k_{obs}, are evaluated. The k_{obs} values at 20 °C obtained in acetonitrile and 6 M HNO_3 (1 M=1 mol dm^{-3}) aqueous solution are summarized in Tables 1 and 2, respectively. In Table 2, the reported rate constants in aqueous solutions are also listed. Agreement between the rate constants in this study and those of pulse radiolysis method by Neta and Huie[9] is better than that with flash photolysis method by Dogliotti and Hayon.[8] With the change of acidity of aqueous solution from 6 M HNO_3 to 2 M HNO_3, appreciable change was not observed. The k_{obs} values in acetonitrile are ca. 10 times larger than the rate constants for hydrogen atom abstraction of $(CH_3)_3CO^{\cdot}$

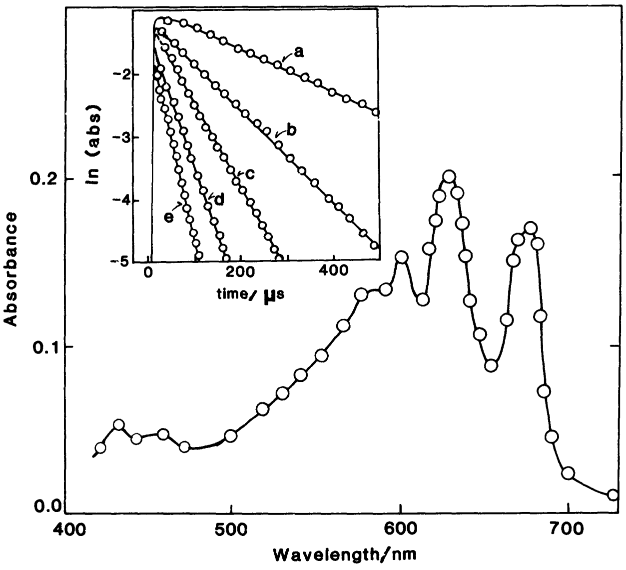


Fig. 1. Transient absorption spectrum observed by flash photolysis of $K_2[Ce(NO_3)_6]$ (10^{-3} mol dm^{-3}). Absorbance at 10 μs after each flash exposure is plotted. Insert: First-order plots for decay of absorbance at 635 nm in acetonitrile (at 20 °C) in the presence of 2-propanol; (a) 0, (b) 0.6, (c) 1.3, (d) 1.9, and (e) 2.5 mmol dm^{-3}.

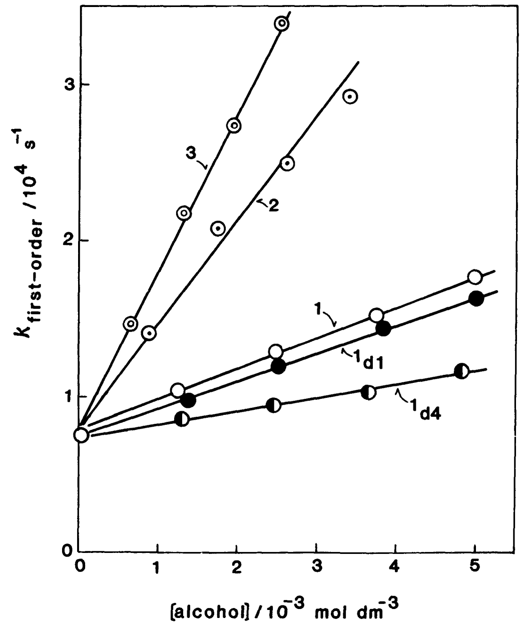


Fig. 2. Pseudo first-order plots for some alcohols in acetonitrile at 20 °C; numbers in figure are referred to as Tables.

Table 1. Rate Constants (at 20 °C) and Arrhenius Parameters for Reactions of $NO_3^{\cdot}$ with Various Alcohols in Acetonitrile;[a)] Bond Dissociation Energy (BDE)[b)] and Ionization Energy (IE)[c)]

	Alcohol	$10^{-6}\,k_{\text{obs}}$ mol^{-1} dm^3 s^{-1}	$10^{-6}\,k_{\text{H}}$ mol^{-1} dm^3 s^{-1}	$\log A_{\text{H}}$	E_{a} kJ mol^{-1}	BDE kJ mol^{-1}	IE eV
1	CH_3OH	2.1	0.70	8.00	11	395	10.85
1$_{\text{d1}}$	CH_3OD	1.9	0.63	7.85	11		
1$_{\text{d4}}$	CD_3OD	0.61	0.20	7.75	14		
2	CH_3CH_2OH	6.7	3.4	8.08	9	390	10.50
3	$(CH_3)_2CHOH$	14	14	8.51	7	382	10.15
4	$(CH_3)_3COH$[d)]	0.23	0.23			441	10.24
			0.03			386	
5	CH_2OHCH_2OH	6.6	1.7	8.20	10		10.55
6	$C_6H_5CH_2OH$	310	160	8.8	<3	348	9.53
7	$CH_2{=}CHCH_2OH$[e)]	260	130	8.7	<3	343	9.63
			260	8.9			

a) Each rate constant contains an estimation error of ±5%; activation energy contains an estimation error of ±1 kJ mol^{-1}. b) Ref. 26. c) Ref. 23. d) Arrhenius parameters were not evaluated because of small $k_{\text{first-order}}$; upper row is for O–H and lower row is for C–H. e) Upper row is for hydrogen-atom abstraction and lower row is for addition reaction.

Table 2. Rate Constants for Reactions of $NO_3^{\cdot}$ with Various Alcohols in Aqueous Solution (6 M HNO_3 at 20 °C)

	Alcohol	$10^{-6}\ k_{obs}$ / $mol^{-1}\ dm^3\ s^{-1}$	$10^{-6}\ k_H$ / $mol^{-1}\ dm^3\ s^{-1}$
1	CH_3OH[a)]	0.31 (0.2,[c)] 1.0[d)])	0.10
1$_{d1}$	CH_3OD	0.30	0.10
1$_{d4}$	CD_3OD	0.15	0.05
2	CH_3CH_2OH	1.2 (1.4,[c)] 3.9[d)])	0.60
3	$(CH_3)_2CHOH$[b)]	2.7 (2.4,[c)] 3.6[d)])	2.7
4	$(CH_3)_3COH$	0.047	0.047
			0.005
5	CH_2OHCH_2OH	0.76	0.19
6	$C_6H_5CH_2OH$.	450	280
7	$CH_2{=}CHCH_2OH$	210	210
		230 (2M HNO_3)	230

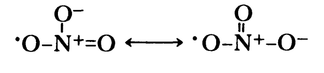
a) $E_a=19\pm2$ kJ mol^{-1}; $\log A_H=8.4\pm0.2$. b) $E_a=11\pm2$ kJ mol^{-1}; $\log A_H=8.6\pm0.2$. c) Pulse radiolysis data (Ref. 9). d) Flash photolysis data (Ref. 8).

from alcohols in organic solvent determined with laser flash photolysis.[17)]

In Fig. 2, it is noticeable that the slope of CH_3OD is practically equal to that of CH_3OH (rate constant is referred to as k^H), whereas that of CD_3OD (k^D) is considerably small. This difference ($k^H/k^D=3.4$) is clearly larger than estimation errors (±5%) which were contained in our method. Although this deuterium-isotope effect is larger than that expected from the primary deuterium-isotope effect ($k^H/k^D=1.63$), further large ratios were reported for the hydrogen-atom abstraction reaction by various radicals.[18)] Especially, the reported ratio (3.2)[17)] for the reaction of $(CH_3)_3CO^{\cdot}$ with 2-propanol is in good agreement with our value. These observations clearly indicate that the reaction path of $NO_3^{\cdot}$ with alcohols with hydrogen atoms at the carbon atom with the OH group is direct hydrogen (deuterium) atom abstraction as shown in Reaction 4.

$$R'R''CHOH + NO_3^{\cdot} \longrightarrow R'R''C^{\cdot}OH + HNO_3 \quad (4)$$

Since the oxygen-centered radicals are known to be highly reactive to hydrogen atom abstraction,[19,20)] the observed large rate constants of $NO_3^{\cdot}$ suggest that $NO_3^{\cdot}$ can be shown in canonical structures I and II, in which an unpaired electron localizes on one oxygen atom.



I II

$$\overset{O^-}{\overset{|}{{}^{\cdot}O{-}N^+{=}O}} \longleftrightarrow \overset{O}{\overset{\|}{{}^{\cdot}O{-}N^+{-}O^-}}$$

In Tables 1 and 2, the rate constants per an active hydrogen (k_H and k_D) are also added by assuming that hydrogen atoms at the α-carbon are predominantly abstracted by $NO_3^{\cdot}$. In the case of 2-methyl-2-propanol (*t*-butyl alcohol), two possible reaction paths (i.e., hydrogen atom abstraction from O–H and from C–H) must be taken into consideration. For 2-propen-1-ol (allyl alcohol), addition reaction mode must be considered besides the hydrogen atom abstraction from allyl position. In each Table, the k_H values increase in the order of $CH_3OH<CH_3CH_2OH<(CH_3)_2CHOH<$benzenemethanol (benzyl alcohol); this order is in good agreement with the reported tendency for other oxygen-centered radicals such as $(CH_3)_3CO^{\cdot}$ and $OH^{\cdot}$.[17–20)]

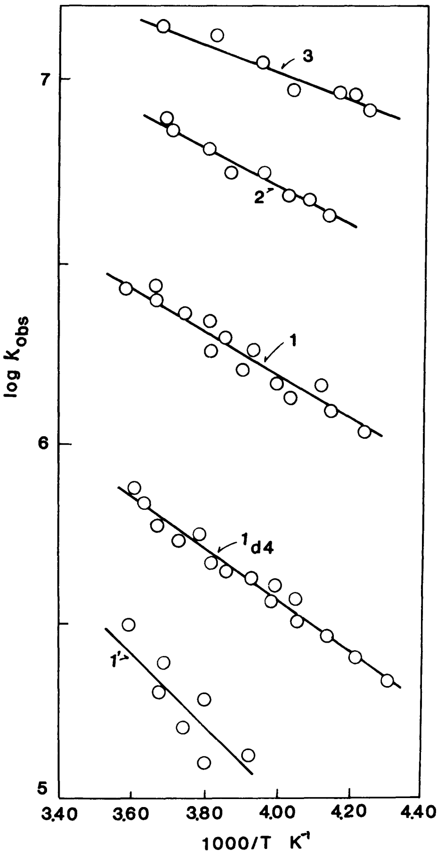


Fig. 3. Arrhenius plots for some alcohols. Numbers are referred to as Tables; **1**′ is for methanol in aqueous solution.

Figure 3 shows the Arrhenius plots for the rate constants for some alcohols between −40 and 20 °C. Fairly good linear lines are obtained for various alcohols. In the case of methanol in acetonitrile, the rate constant at 20 °C is about three times larger than that at −40 °C. In Table 1, the activation energies (E_a) and frequency factors per an active hydrogen atom ($\log A_H$) obtained in acetonitrile are summarized. By the variation of ±1 kJ mol^{-1} in E_a, the A value varies ±30%; thus, they are shown in the form of $\log A$. The E_a values for aliphatic alcohols seem to be smaller than the reported values for the carbon-centered radicals.[19] In the reported activation energies, we can find a tendency that the activation energies for the hydrogen-atom abstraction reactions by the oxygen-centered radicals are smaller than those by other radicals.[19] For example, the reported E_a value of 22.2 kJ mol^{-1} for $(CH_3)_3CO^{\cdot}$-methanol is comparable with our value for $NO_3^{\cdot}$ by taking smaller rate constant for $(CH_3)_3CO^{\cdot}$ (1.3×10^5 mol^{-1} dm^3 s^{-1}) into consideration.[21]

In Table 1, the E_a values decrease with an increase in the k_H values, showing linear free energy relationship.[19] With the increase in the k_H values, the $\log A_H$ values seem to increase. The reactivity at ambient temperature is determined by the combination of both E_a and A.

In Fig. 4, the rate constants in acetonitrile are plotted against the rate constants in aqueous solution. In the range of k_H smaller than 10^8 mol^{-1} dm^3 s^{-1}, the rate constants in acetonitrile are larger than the corresponding rate constants in aqueous solution by a factor of ca. 10. This difference may be attributed to the interaction between the attacking radical and acidic aqueous solvent via hydrogen bond. From the canonical structures of $NO_3^{\cdot}$ (**I** and **II**), the electron-deficient oxygen radical center may interact with oxygen atom of H_2O. Such interaction may interfere the approach of alcohols to $NO_3^{\cdot}$. In addition, the hydrogen bonds between alcohols and H_2O also tend to decrease the reaction rates.

For benzyl alcohol, the rate constants in both solvents approach to the same value. Interchange of the reaction modes from hydrogen atom abstraction was not expected, since the rate constant of benzyl alcohol is similar to that of toluene, in which benzylic hydrogen atom is abstracted.[7,22] Taking the high ionization energy of benzyl alcohol into consideration,[23] electron-transfer reaction is not probable. Addition of $NO_3^{\cdot}$ to the benzene ring is not probable, because the reactivity for addition to the phenyl ring is low.[12] Thus, the approach of the rate constants in the both solvents suggests the reactivity-selectivity principle;[24] for fast reactions, selectivity is reduced. Indeed, the rate constants are only ca. 1/10 of the diffusion controlled limits in the both solvents.[25] In the case of allyl alcohol, although the addition reaction of $NO_3^{\cdot}$ to the double bond must be taken into consideration, the similar behavior was found.

In Fig. 5, the rate constants ($\log k_{obs}$ and $\log k_H$) in acetonitrile are plotted against the bond-dissociation energies between C–H at the α-position; for *t*-butyl alcohol, the plot for O–H is also shown. A general tendency was found, showing that the reactivities of alcohols increase with a decrease in the bond-dissociation energies.[26] Since the reactivities of alcohols are correlated linearly with the bond-dissociation energy at C_α–H, the reaction mode was confirmed to be Reaction 4. For *t*-butyl alcohol, the rate constant plotted against the bond-dissociation energy for O–H is found near the extrapolated line for $\log k_{obs}$ and for $\log k_H$. The reported ESR spectra support the hydrogen-atom

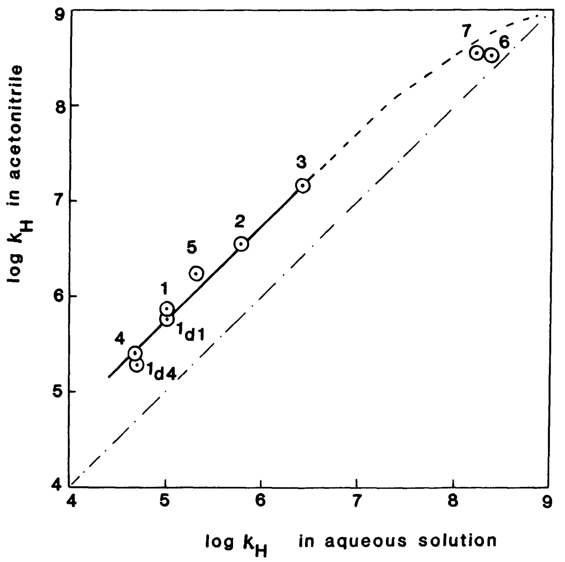


Fig. 4. Correlation between $\log k_H$ in acetonitrile and $\log k_H$ in 6 M HNO_3 at 20°C.

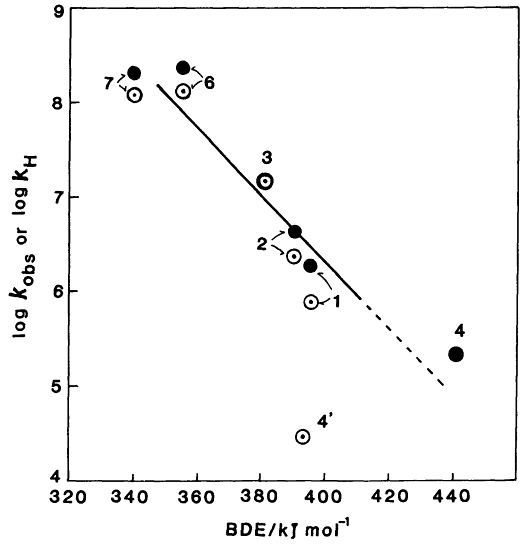


Fig. 5. $\log k_{obs}$ (●) or $\log k_H$ (⊙) at 20°C in acetonitrile vs. bond-dissociation energy (BDE); **4** is for BDE(O–H) and **4′** for BDE(C–H).

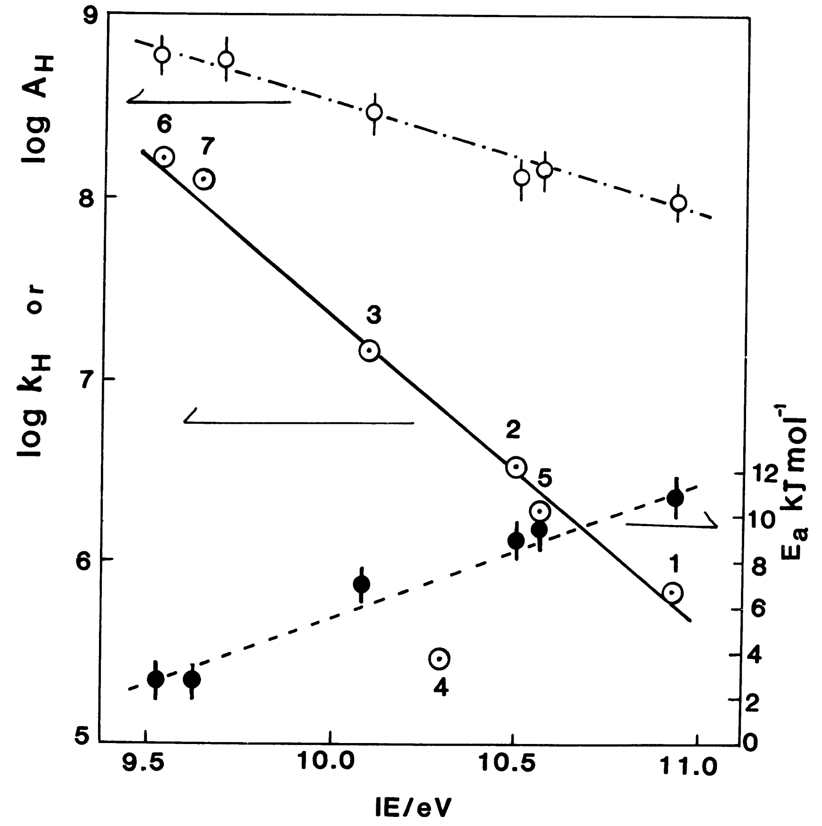


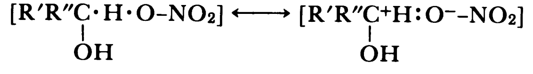
Fig. 6. log k_H (⊙), log A_H (○), and E_a (●) at 20 °C in acetonitrile vs. ionization energy (IE).

abstraction reaction from the OH group [Reaction 5].[1–3)]

$$R_3COH + NO_3^{\bullet} \longrightarrow R_3CO^{\bullet} + HNO_3 \qquad (5)$$

In the case of allyl alcohol, since the rate constant is found near the line, the hydrogen-atom abstraction reaction from allylic position was suggested.

Figure 6 shows the plot of log k_H, log A_H, and E_a, against the ionization energies of alcohols.[23)] Fairly good linear relationship is found for log k_H of alcohols except *t*-butyl alcohol. There seems to be a general tendency that the reactivity increases with a decrease in the ionization energy. This suggests a high electrophilicity of $NO_3^{\bullet}$, which is in good agreement with the reported high electron affinity (3.5 eV).[27)] Furthermore, it is indicated that there are contributions of the polar resonance structures to the transition state; charge transfer from alcohols to $NO_3^{\bullet}$ occurs in the transition state as shown by **III** and **IV**.[18)] By the contribution of these polar resonance structures, it is expected that the activation energy is decreased; indeed, a decrease in E_a with a decrease in the ionization energy was seen in Fig. 6.



$$[R'R''\underset{OH}{\dot{C}}\cdot H\cdot O\text{-}NO_2] \longleftrightarrow [R'R''\underset{OH}{\dot{C}^+}H{:}O^-\text{-}NO_2]$$

III **IV**

The log A_H values are also influenced by the ionization energies of alcohols, suggesting that polar effect also presents in the orientation factor.[12)]

The slightly lower reactivity of 1,2-ethanediol than that of ethanol is attributed to its higher ionization energy. Downward deviation of k_H of *t*-butyl alcohol suggests a different reaction mode having less polar transition state. The hydrogen atom of the OH group in *t*-butyl alcohol is more electron-deficient than that of C–H; thus, Reaction 5 proceeds via less polar transition state.

Although the point for allyl alcohol in Fig. 6 is on a line for the hydrogen-atom abstraction [Reaction 4], one can not exclude a possibility of addition reaction path, because the rate constant for vinyl acetate (2.5×10^8 mol^{-1} dm^3 s^{-1} at 5 °C in acetonitrile),[28)] which is a nonconjugate vinyl monomer similar to allyl alcohol, is close to that of allyl alcohol.

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