Chemically Induced Dynamic Electron Polarization Study of the Rates of Hydrogen Abstraction Reactions of Carbonyls. Position Dependence and Deuterium Effect

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Using time-resolved EPR, we have investigated the hydrogen abstraction reaction of carbonyls, especially acetone, with alkanes and 2-propanol to examine the position and type dependence of the reaction and the reaction mechanism. It is concluded that all the secondary hydrogens at different positions of alkanes are abstracted at almost equal rates, which cannot be explained by a simple MO theory. The results for the reactivities of the hydrogens of the different types are consistent with related studies, i.e., $k_1/k_2 \le 0.1$ and $k_2/k_3 \simeq 0.1$, where k_1 , k_2 , and k_3 are abstraction rate constants for primary, secondary, and tertiary hydrogens, respectively. As for the deuterium isotope effects on the reaction rates of acetone and cyclopentanone with 2-propanol, $k_{\rm H}/k_{\rm D}$, are found to be around 3-4 with no significant temperature dependence. The implication of this result is briefly discussed.

Introduction

The time-resolved EPR (TREPR) technique with a time resolution of submicroseconds is suitable for investigation of transient paramagnetic species.^{1,2} By observing hyperfine structures, one can easily identify the transient radicals that cannot be distinguished by other techniques. Transient radicals produced by photolysis or radiolysis have anomalous electron spin polarization, so-called chemically induced dynamic electron polarization (CIDEP), just after the formation of the radicals.¹ Detection of transient radicals is greatly facilitated by the enhanced intensities due to CIDEP. We have previously applied the TREPR technique to investigate various transient radicals produced by hydrogen abstraction reactions of aliphatic carbonyls and studied CIDEP mechanisms,^{3,4} reaction pathways,⁵ and radical pairs.^{6,7} In the present work we have studied the problems related to the hydrogen abstraction rate constants.

The hydrogen abstraction reaction is one of the basic photochemical processes and has been the subject of a number of investigations.⁸⁻²⁰ Rate constants of numerous hydrogen abstraction reactions have been obtained by product analysis,¹⁵ flash photolysis,¹⁶⁻¹⁹ and other methods.^{9-11,19,20} The hydrogen abstraction reactions of carbonyls are the typical examples and have attracted much attention. There are two interesting questions about these reactions. The first is the question about the difference among the reactivities of the different kinds of hydrogens of the donor molecule. It has been predicted on the basis of a simple MO calculation that the reactivities of the different kinds of hydrogen are different in *n*-pentane.²¹ It is, however, difficult to examine this experimentally, because we cannot distinguish the transient absorptions of the alkyl radicals produced by the abstraction of different kinds of hydrogens. Nevertheless, one often interpret the reaction rate on the assumption that the hydrogens of the same type are abstracted at equal rates. The reactivities of the different kinds of hydrogens have been discussed based on the data obtained for different molecules, but direct comparison within the same molecule is desirable. The second question is concerned with the reaction mechanism. Scaiano et al.¹² and Topp¹⁶ discussed the reaction rate constants on the basis of the classical thermal activation process, whereas Formoshinho et al. suggested a tunneling mechanism for this reaction.¹³ Therefore, this question does not seem to have been settled. To determine the mechanism, it is important to have data on the deuterium isotope effect on the rate constants over a wide range of temperature, but we lack such data.

Here we show that the analysis of the CIDEP spectra can provide information about the reaction rate constants. Although absolute rate constants cannot be obtained from the CIDEP

spectra, the ratio of the rates of two reactions occurring under the same condition can be estimated by comparing the signal intensities. We have applied this method to provide data on the questions about the hydrogen abstraction reactions mentioned above. Since the CIDEP mechanisms operative in the reactions of carbonyls, especially acetone, are now well understood,^{3,4} the CIDEP spectra of the transient radicals produced by the hydrogen abstraction reactions can be analyzed easily. Here, we first examine the CIDEP spectra of the transient alkyl radicals produced by the photolysis of carbonyls in various alkanes. Then we determine the position dependence of the hydrogen abstraction rate, i.e., the difference in the reactivities among the secondary hydrogens and the different types of hydrogens in the identical molecule. Next we examine the CIDEP spectra of acetone and cyclopentanone in a 1:1 mixture of 2-propanol- h_8 and 2propanol- d_8 and determine the deuterium isotope effect on the abstraction reaction rate constants over a wide range of temperature. Finally the observed results are compared with the results of the related studies and the theoretical predictions.

Experimental Section

The details of the time-resolved EPR spectrometer and the experimental procedure were reported elsewhere.⁴ The excitation

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Figure 1. (a) CIDEP spectrum for acetone in *n*-decane at 0.8 μ s after the laser excitation and 6 °C. The time evolutions of the peaks indicated by arrows in the figure are shown in Figure 6. (b) The simulated intensities of the spectra of the alkyl radicals (A and B radicals in a) consist of the contributions of ST₀M and TM.

source was a Lumonics EX400 excimer laser with a XeCl fill ($\lambda = 308 \text{ nm}$ and $\sim 300 \text{ mJ/pulse}$). Temperature was stabilized by flowing cold nitrogen gas. Acetone, normal and cyclic alkanes, 2-propanol, and chloromethane (Wako Pure Chemicals) of spectrograde and acetone- d_6 and 2-propanol- d_8 (Aldrich), benzophenone, acetophenone, benzaldehyde, xanthone, 2,3-dimethylbutane, 2,4-dimethylpentane, and hexamethylethane (Nacalai Tesque) of the highest grade were used without further purification. The concentrations of acetone and other carbonyls were 1 and 0.1 M, respectively.

Result and Interpretation

Spectra of Acetone in Alkanes. Figure 1a shows the CIDEP spectrum of acetone in *n*-decane $(n-C_{10})$ obtained at 6 °C and 0.8 μ s after the laser excitation. The spectrum has a S/N ratio (~50) acceptable for a quantitative discussion. Sharp and strong signals belong to the isopropyl ketyl radical ((CH₃)₂COH) with a hyperfine coupling constant (hfcc) of the methyl protons of 19.2 G. The other signals indicated by arrows belong to the alkyl radicals. These radicals were produced by the hydrogen abstraction reaction from *n*-C₁₀ by acetone in the excited triplet state. The photochemical reaction is given as

$$(CH_3)_2CO^* + C_{10}H_{22} \rightarrow (CH_3)_2\dot{C}OH + \dot{C}_{10}H_{21}$$
 (1)

The produced alkyl radicals are classified into two types: one is produced by the abstraction of hydrogens (A hydrogens) bonded to the carbon atoms next to the terminal carbon atoms (-CH₂ĊHCH₃; A radical), and the other is produced by the abstraction of other secondary hydrogens (B hydrogens, -CH₂-ĊHCH₂-; B radical). Hfcc's of γ -protons are so small (<1 G) that we cannot differentiate the B radicals further. It is notable that the radicals produced by the abstraction of the primary hydrogens were not observed in the CIDEP spectrum. The spectrum shows an E/A* pattern (E/A + A; E/A, and A denote a microwave emission on the low-field side and absorption on the high-field side and a net absorption, respectively). These E/A



Figure 2. CIDEP spectra for (a) acetone- d_6 and in *n*-pentadecane and (b) acetone- h_6 in dimethylbutane.

TABLE I:	Hyperfine	Coupling	Constants of	i the	Alkyl	Radicals ⁴
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Normal Alkanes					
-CH		CHCH2-	-CH2CHCH3		
alkane	a _{CH} ^α	4a _{CH2} ^β	a _{CH} ^a	2a _{CH2} ^β , 3a _{CH3} ^β	
n-C ₅	22.3	24.7	20.8	24.8	
$n-C_6$	22.4	26.1	21.4	24.6	
$n-C_7$	20.8	25.0	21.7	24.3	
$n-C_8$	20.8	24.4	20.9	24.3	
n-C ₉	20.9	24.6	21.0	24.4	
n-C10	21.2	24.7	21.5	24.5	
$n-C_{12}$	22.2	24.2	21.4	24.4	
$n-C_{15}$	21.1	24.7	21.4	24.4	
	F	Branched All	canes		
(CH ₃) ₂ ĊC	$H(CH_3)_2^b$	a _{CI}	$\mu^{\beta} = 12.0,$	$6a_{\rm CH}^{\ \beta} = 22.9$	
(CH ₃) ₂ CC	H ₂ CH(CH	$_{3})_{2}^{b}$ $2a_{1}^{b}$	$_{\rm CH}^{\ \ \beta} = 16.7$	$7, 6a_{\rm CH},^{\beta} = 23.0$	
(CH ₃) ₂ CH	ĊĦCH(Cł	$(1_3)_2^b$ 2a	$_{\rm CH}^{\beta} = 22.7$	$a_{\rm CH}^{a} = 23.0$	
		Cyclic Alka	nes		

$(CH_2)CH(CH_2)_3(CH_2)$	$a_{\rm CH}^{\alpha} =$	20.8,	2a _{CH} ^β	=	45.2

^aThe g values of all the alkyl radicals are 2.0026. The unit of the hyperfine coupling constants is gauss. ^bThe hyperfine coupling constants of the radicals were obtained for the first time in this work.

and A patterns are interpreted by the radical pair mechanism (RPM) involving the $S-T_0$ mixing (ST_0M) and the triplet mechanism (TM), respectively, as already shown in the previous paper.³

Spectra in other normal alkanes $(n-C_n, n = 5-9, 12, \text{ and } 15)$ as solvents are similar to that of $n-C_{10}$, except for the relative intensities of the signals, which results from the difference in the contributions of the two mechanisms due to the difference of the viscosities of alkanes.^{3,22} The spectrum of acetone- d_6 is also shown in Figure 2a. In the spectrum of 2,3-dimethylpentane (DMP), the radicals produced by the abstraction of both the secondary and tertiary hydrogens (secondary and tertiary radicals, respectively) were observed. The radical produced by the abstraction of the primary hydrogen (primary radical) was not observed. Similarly, only the tertiary radical was observed in the system of 2,3-dimethylbutane (DMB, Figure 2b). We summarize hfcc's obtained for the transient alkyl radicals in Table I. Some of them

⁽²²⁾ CRC Handbook of Chemistry and Physics, 68th ed.; CRC Press: Boca Raton, FL; pp F-39-F-43.



Figure 3. (a) CIDEP spectrum for acetone- h_6 in a mixture of 2-propanol- h_8 and 2-propanol- d_8 (1:1). (b) Magnified spectrum of (a).



Figure 4. (a) CIDEP spectrum for acetone- d_6 in a mixture of 2-propanol- h_8 and 2-propanol- d_8 (1:1). (b) Magnified spectrum of (a).

have already been determined from the studies of the peroxide decomposition by radiolysis and photolysis in solution.²³ Our values are consistent with those reported.

Spectra of Acetone and Cyclopentanone in a Mixed Solvent. The spectrum of acetone- h_6 in a mixture of 2-propanol- h_8 and 2-propanol- d_8 (1:1) at -20 °C is shown in Figure 3. In this mixture the isopropyl ketyl radical and its deuterated radicals ((CD₃)₂COD and (CH₃)₂COD) produced by reactions 2 and 3

$$(CH_3)_2CO^* + (CH_3)_2CHOH \rightarrow 2(CH_3)_2\dot{C}OH$$
 (2)

$$(CH_3)_2CO^* + (CD_3)_2CDOD \rightarrow (CH_3)_2\dot{C}OD + (CD_3)_2\dot{C}OD$$
(3)

give rise to the observed CIDEP spectrum. The spectrum has a S/N ratio sufficiently large for a quantitative analysis. In the spectrum two radicals, $(CH_3)_2$ ·COH and $(CH_3)_2$ ·COD, cannot be distinguished because of the small hydroxyl proton splitting, so the two ketyl radicals are called "hydrated radicals". The spectrum shows an E/A^* pattern, and the A pattern decreases its intensity with lowering temperature as reported previously.⁴ The investigated temperature range was from room temperature (19 °C) to -41 °C.

In the photolysis of acetone- d_6 in the mixture, a similar spectrum is observed (Figure 4). Deuterated radicals ((CD₃)₂COD and (CD₃)₂COH) formed by reactions 4 and 5 give the deuterated spectrum with a strong intensity.

$$(CD_3)_2CO^* + (CD_3)_2CDOD \rightarrow 2(CD_3)_2\dot{C}OD \qquad (4)$$

$$(CD_3)_2CO^* + (CH_3)_2CHOH \rightarrow (CD_3)_2\dot{C}OH + (CH_3)_2\dot{C}OH$$
(5)



Figure 5. Time evolutions of the EPR signals of (a) A radical and (b) B radical indicated by arrows in Figure 1a.

Temperature dependence (-3 to -43 °C) of the spectrum for cyclopentanone in the mixture of 2-propanol was also examined. The spectrum shows the cyclopentyl, isopropyl, and their deuterated ketyl radicals. Observed reactions are given as

$$OC(CH_2)_3CH_2^* + (CH_3)_2CHOH \rightarrow HOC(CH_2)_3CH_2 + (CH_3)_2COH (6)$$
$$OC(CH_2)_3CH_2^* + (CD_3)_2CDOD \rightarrow DOC(CH_2)_3CH_2 + (CD_3)_2COD (7)$$

Two kinds of cyclopentyl radicals cannot be distinguished in the spectrum.

Analysis

In this section we describe a method for the analysis of the CIDEP spectrum to investigate the relative reactivity. We first illustrate the analysis of the reactions of alkanes in detail, and the position and type dependence of the hydrogen abstraction reaction are then examined. Next, we examine the deuterium isotope effect using the same method.

Position and Type Dependence. (a) Reactivity of the secondary hydrogens of alkanes: Figure 5 shows the decays of the EPR signals of the A and B radicals, which were observed with a low microwave power of 0.1 mW to avoid an influence of nutation on the decay curves. These decay processes are considered to be determined by the spin-lattice relaxation process, and their relaxation times are nearly the same, being a few microseconds (~ 4 μ s). Therefore, the signal intensities observed at 0.8 μ s after the laser excitation can safely be considered to reflect the concentrations of the radicals just after their formation, which are proportional to the rates of the hydrogen abstraction. As we described in the previous section, the observed CIDEP spectrum consists of those due to the two mechanisms, ST₀M and TM. Therefore, an integrated intensity of the *i*th peak (*i*, nuclear magnetic quantum number), I(i), is given by a summation of the two contributions $(I_{ST_0M}(i) \text{ and } I_{TM}(i))$:

$$I(i) = I_{\mathrm{ST}_0\mathrm{M}}(i) + I_{\mathrm{TM}}(i) \tag{8}$$

The CIDEP spectrum can be simulated in terms of the sum of the contributions of ST_0M and TM in the following fashion:^{3,4} The relative intensities of these peaks were estimated from the theoretical formulas for each mechanism.¹ For TM this ratio is simply estimated from their state degeneracies because the polarization intensity due to TM, $P_{TM}(i)$, is independent of the nuclear state. As for ST_0M , the polarization intensity due to

TABLE II: Ratio of the Reaction Rate Constants of Acetone k_B/k_A^a

alkane	$k_{\rm B}/k_{\rm A}$	alkane	$k_{\rm B}/k_{\rm A}$	
n-C ₆	1.25 ± 0.3^{b}	<i>n</i> -C ₁₀	1.05 ± 0.2	
$n-C_{7}$	1.10 ± 0.3	$n-C_{12}$	0.85 ± 0.15	
$n-C_8$	1.05 ± 0.2	$n-C_{15}$	0.90 ± 0.15	
n-C	1.00 • 0.2		0.95 单 0.15°	
,	1.00 ♠ 0.2°			

"The experiment was done at 6 °C. b The error bars were estimated from the S/N ratios of the spectra. The value for acetone- d_6 .

 ST_0M , $P_{ST_0M}(i)$, can be approximately calculated by the equations^{24,25}

$$P_{\mathrm{ST}_{0}\mathrm{M}}(i) \propto \sum_{b} \operatorname{sign} (Q_{\mathrm{ab}}) |Q_{\mathrm{ab}}|^{0.5}$$
(9)

$$Q_{ab} = \frac{1}{2}(g_1 - g_2)\beta H + \frac{1}{2}(\sum_{p}^{a}A_{1p}m_{1p} - \sum_{q}^{b}A_{2q}m_{2q}) \quad (10)$$

where p and q refer to the different nuclei in radicals 1 and 2, which are in the overall nuclear states a and b. In these cases, radical 2 is the isopropyl ketyl radical with $A_{CH_3} = 19.2$ G and $g_2 = 2.0030$, and radical 1 is the A radical with $A_{\rm H}^{\alpha} = 21.3$ G, $A_{\rm H}^{\beta} = 24.5$ G, and $g_1 = 2.0026$ or the B radical with $A_{\rm H}^{\alpha} = 21.6$ G, $A_{\rm H}^{\beta} = 24.9$ G, and $g_1 = 2.0026$. By using these values and eqs 9 and 10, we obtain the E/A spectra with the ratios of -6.01:-3.86:-6.98:-0.68:1.16:7.30:4.00:6.11 for the central eight peaks of the A radical from the low field to the high field and -2.06:-7.69:-3.18:-3.83:4.12:3.43:7.90:2.15 for the central eight peaks of the B radical. The minus sign denotes the microwave emission. We show the simulation of the spectrum in terms of the two contributions as shown in Figure 1b.

Both $I_{ST_0M}(i)$ and $I_{TM}(i)$ obtained by the simulation can be expressed as

$$I_{\text{ST}_0M}(i) \propto P_{\text{ST}_0M}(i)k \text{ deg } (i)n \tag{11}$$

$$I_{\text{TM}}(i) \propto P_{\text{TM}}(i)k \deg(i)n$$
 (12)

where k, deg (i), and n denote the reaction rate constant per hydrogen atom, the nuclear degeneracy of the *i*th state, and the number of the hydrogen atoms that can be abstracted to produce the A or B radicals, respectively. deg (i) is normalized so that the sum of deg (i) over all i values is unity.

Because $I_{TM}(i)$'s are smaller than $I_{ST_0M}(i)$'s in our system, we estimate k from $I_{ST_0M}(i)$. We obtained the ratio of the rate constants for the formation of the A and B radicals, $k_{\rm B}/k_{\rm A}$, by averaging k estimated from the intensity of each peak in Figure 1a. We summarize the result in Table II. It should be noted that $k_{\rm B}$ represents the rate constant averaged over all the secondary hydrogens except the A hydrogens. The values of k_B/k_A are also estimated for the systems of acetone- d_6 by using $A_{CD_3} = 2.9 \text{ G}$ (Table II). All of the values obtained for $k_{\rm B}/k_{\rm A}$ are close to unity within experimental errors. Therefore, it is indicated that all the secondary hydrogens of alkanes are abstracted by excited triplet acetone at almost equal rates, $k_{\rm B}/k_{\rm A} \simeq 1$. We also estimated $k_{\rm B}/k_{\rm A}$ from $I_{\rm TM}(i)$ in the *n*-C₆ system where the contribution of TM is relatively large as compared with the other normal alkanes. $k_{\rm B}/k_{\rm A}$ is estimated to be 1.2 ± 0.3, which is in good agreement with the results obtained from $I_{ST_0M}(i)$. Thus it is shown for the first time that the reactivity of the secondary hydrogens of normal alkanes does not depend on the position significantly.

(b) Reactivities of the different types of hydrogens of alkanes: We next examine the reactivities among the primary, secondary, and tertiary hydrogens. The fact that the primary radical was not detected in the CIDEP spectra suggests that the abstraction rate of the primary hydrogen, k_1 , is negligibly small compared with those of the secondary ones, k_2 . To investigate the reactivity of the primary hydrogen, we examined the reaction of acetone



Figure 6. CIDEP spectra for (a) xanthone, (b) benzaldehyde, (c) acetophenone, and (d) benzophenone in n-pentadecane.

with hexamethylethane (HME) which has only primary hydrogens. We observed the CIDEP signal neither of the isopropyl ketyl radical nor of the alkyl radicals in the photolysis of acetone (1 M) and HME (1 M) in chloromethane, whereas we observed the signals of both radicals in the system of acetone and $n-C_{12}$ (1 M) in the same solvent. We also checked that the photolysis of acetone in this solvent provided no CIDEP signal of the isopropyl ketyl radical under the same condition. This result indicates less reactivity of the primary hydrogen and

$$k_1/k_2 \le 0.1$$
 (13)

where the upper limit is estimated from the S/N ratio of the spectrum. The ratio of the rate constants between the secondary and the tertiary hydrogens, k_2/k_3 , was obtained from the analyses of the spectra of acetone- h_6 in DMP and acetone- d_6 in DMP as

$$k_2/k_3 \simeq 0.1 \tag{14}$$

There is a rather large uncertainty in this case since the spectrum of the secondary radical has a weak intensity. In the spectrum for DMB only the tertiary radical was observed, indicating a large k_3 compared with k_1 . From the S/N ratio the following relation was obtained:

$$k_1/k_3 \le 0.01$$
 (15)

This relation is consistent with eqs 13 and 14.

(c) Other carbonyls in alkanes: We examined other carbonyls such as benzophenone (BP), benzaldehyde, acetophenone, and xanthone in $n-C_{15}$ (Figure 6). The spectra show the A and B radicals. For BP we obtained $k_{\rm B}/k_{\rm A} = 1.2 \pm 0.2$ and 1.0 ± 0.3 in $n-C_{15}$ and $n-C_6$, respectively, by an analysis similar to those given in the previous section using hfcc of the BP ketyl radical of $A_{OH} = 2.91$ G, $A_{H}^{ortbo} = 3.21$ G, $A_{H}^{meta} = 1.23$ G, and A_{H}^{para} = $3.65 \text{ G}.^{23}$ Since the relative intensities of the signals of the A and B radicals in the spectrum are almost the same for all the carbonyls examined here, we conclude that $k_{\rm B}/k_{\rm A}$ does not depend on the nature of the hydrogen acceptor.

To determine k_2/k_3 , we studied a reaction of BP with DMP. We observed the BP ketyl, secondary, and tertiary radicals but not the primary radicals in the spectrum as in the case of acetone. We estimated the ratio of the rate constants as $k_2/k_3 = 0.1$ in a similar fashion.

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TABLE III: Deuterium Isotope Effect on the Reaction of Acetone with 2-Propanol

<i>T/</i> °C	$k_{\rm H}/k_{\rm D}$	T/°C	$k_{\rm H}/k_{\rm D}$	
19	4.1 ± 0.8^{a}	-20	3.5 ± 0.7	
-2	3.5 ± 0.7	-41	4.0 ± 0.8	

"The error bars were estimated from the S/N ratios of the spectra.

TABLE IV: Deuterium Isotope Effect on the Reaction Rate of Cyclopentanone in 2-Propanol

T/°C	$k_{\rm H}/k_{\rm D}$	T/°C	$k_{\rm H}/k_{\rm D}$	
-3	3.0 ± 0.6^{a}	-32	3.2 ± 0.6	
-22	2.8 ± 0.6	-43	3.1 ± 0.6	

"The error bars were estimated from the S/N ratios of the spectra.

Deuterium Isotope Effect. The spectra in the mixture of 2propanol are similarly investigated. In the temperature range investigated here ST_0M and TM contribute to the spectrum as described previously.^{3,4} The contribution of ST_0M is estimated from the simulation of the spectrum. The integrated signal intensities due to ST_0M for the hydrated and deuterated radicals can be expressed as

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$$I^{\mathrm{H}}(i) \propto (2k_{\mathrm{H}}P^{\mathrm{H}}(i;\mathrm{H}) + k_{\mathrm{D}}P^{\mathrm{H}}(i;\mathrm{D})) \operatorname{deg}(i)$$
(16)

$$\mathbf{P}(i) \propto k_{\mathrm{D}} P^{\mathrm{D}}(i;\mathrm{H}) \deg(i)$$
 (17)

Here *i* denotes the nuclear quantum number. $P^{D}(i;H)$ is the polarization intensity in the *i*th nuclear state of the deuterated radical due to $ST_{0}M$ in the case where the hydrated radical is radical 2. The other symbols for the polarization, $P^{H}(i;H)$ and $P^{H}(i;D)$, have the corresponding meanings. The polarization such as $P^{D}(i;H)$ is calculated in terms of eqs 9 and 10. The value of k_{H}/k_{D} is obtained for each temperature by averaging the values obtained from all the signals in the spectrum. The results for the temperature dependence of k_{H}/k_{D} are summarized in Table III. As seen from the table, the ratios take values around 4 and show almost no temperature dependence.

In the case of acetone- d_6 as a solute the integrated signal intensities for the hydrated and deuterated radicals are given as

$$I^{\rm H}(i) \propto k_{\rm H} P^{\rm H}(i; {\rm D}) \, \deg(i) \tag{18}$$

$$I^{\mathsf{D}}(i) \propto (k_{\mathsf{H}} P^{\mathsf{D}}(i;\mathsf{H}) + 2k_{\mathsf{D}} P^{\mathsf{D}}(i;\mathsf{D})) \operatorname{deg}(i)$$
(19)

The value of $k_{\rm H}/k_{\rm D}$ is estimated to be 4.2 at 19 °C, which is in a good agreement with the result for acetone- h_6 .

As for the reaction of cyclopentanone with 2-propanol, the ratio of $k_{\rm H}/k_{\rm D}$ is estimated by analyzing the signals of the deuterated and hydrated isopropyl ketyl radicals similarly:

$$I^{\mathbf{D}}(i) \propto k_{\mathbf{D}} P^{\mathbf{D}}(i; \mathbf{c} \cdot \mathbf{C}_{5}) \operatorname{deg}(i)$$
(20)

$$I^{\rm H}(i) \propto k_{\rm H} P^{\rm H}(i; \text{c-C}_5) \deg(i)$$
(21)

As shown in Table IV, the value of $k_{\rm H}/k_{\rm D}$ has little temperature dependence, taking a value around 3.

Here we comment on the method of the analysis. In the case of cyclopentanone, the evaluation of the ratio is straightforward; $k_{\rm D}$ and $k_{\rm H}$ are estimated from the analyses of the deuterated and hydrated radicals, eqs 20 and 21, respectively. For acetone, however, a simultaneous equation (eqs 16 or 19) has to be solved to obtain the reaction rates. Since $k_{\rm H} > k_{\rm D}$, the terms with $k_{\rm H}$ are dominant in eqs 16 and 19. Consequently, the values of $k_{\rm D}$ obtained from eqs 16 and 19 have considerable experimental errors. Therefore, to get the temperature dependence of $k_{\rm H}/k_{\rm D}$, we analyze the spectrum of acetone- h_6 , where $k_{\rm D}$ is evaluated straightforwardly from eq 17.

Discussion

Comparison with the Related Studies. As for the value of k_B/k_A , there are no experimental data to be compared with ours to the best of our knowledge. The reactivities of the different types of hydrogens were examined in different alkanes. As for acetone, Porter et al. obtained the total rate constants of the hydrogen



Figure 7. Values of the frontier electron densities in the hydrogen atoms of (a) *n*-pentane from ref 21, (b) *n*-decane, and (c) *n*-pentadecane.

abstraction from alkanes, k, by measuring the rise time of the isopropyl ketyl radical in the flash photolysis as $k = 2.4 \times 10^5$, 3.4×10^5 , 1.8×10^5 , and $6 \times 10^4 \text{ s}^{-1} \text{ M}^{-1}$ for c-C₅, c-C₆, n-C₆, and HME, respectively.¹⁷ The relative rate constants of the primary and secondary hydrogens were approximately estimated as $k_1/k_2 \simeq 0.1$, which is consistent with our result. In the case of BP, Giering et al. obtained $k_1 = 1.7 \times 10^3 \text{ s}^{-1} \text{ M}^{-1}$, $k_2 = 6.0 \times 10^4 \text{ s}^{-1} \text{ M}^{-1}$, $k_3 = 5.7 \times 10^5 \text{ s}^{-1} \text{ M}^{-1}$, giving $k_1/k_2 \simeq 0.03$ and $k_2/k_3 = 0.13$ by using the Stern-Volmer plots and direct measurements of the triplet lifetimes.¹⁹ Walling and Gibian estimated k_2/k_3 to be 0.16 by the product analysis.¹⁵ These results obtained with various kinds of alkanes are in good agreement with our results obtained within identical molecules.

Comparison with MO Calculation. The MO calculation has been useful in interpreting reactivities of many systems including photochemical reactions. Fukui et al. proposed that the frontier electron density would give a good indication for the reactivity in the hydrogen abstraction reaction. They calculated the frontier electron densities for normal and branched alkanes by the Hückel MO method for the σ -bonds.²¹ The relevant frontier electron density is defined as a sum of the electron densities in the highest occupied and lowest unoccupied molecular orbitals:

$$\rho_{\rm f} = (C_{\rm HOMO})^2 + (C_{\rm LUMO})^2$$
(22)

In calculating the MOs the resonance integrals are set as follows: the resonance integrals between the two sp³ orbitals of the two adjacent carbon atoms, between the sp³ orbital of the carbon and the 1s orbital of hydrogen in the C-H bond, and between the two sp³ orbitals belonging to the same carbon atom, are β , 1.1 β , and 0.34β , respectively. The Coulomb integrals of the carbon and hydrogen atoms are taken as α and $-0.2\beta + \alpha$, respectively. All the overlap integrals are neglected. Figure 7a shows their result for $i-C_5$. According to their interpretation, the more frontier electron density the hydrogen has, the higher its reactivity for the hydrogen abstraction reaction. The result indicates qualitatively $k_3 > k_2 > k_1$, though a quantitative comparison of the reactivity is difficult due to the crudeness of the approximation. This tendency is consistent with ours. In the calculation of $n-C_5$ they showed that the inner secondary hydrogens have more frontier electron densities than the outer ones. We performed similar calculations for $n-C_{10}$ and $n-C_{15}$. The results are shown in Figure 7b,c. The reactivities of the inner secondary hydrogens are predicted to be higher than those of the outer ones, but we did not find any experimental evidence to support this prediction. It seems that the simple Hückel method is not suitable for discussing the difference in the reactivities of the secondary hydrogens.

Deuterium Isotope Effect. Our values of $k_{\rm H}/k_{\rm D}$ for acetone and cyclopentanone at room temperature are 4.1 and 3.0, respectively. Yip and Siebrand measured the deuteration effect on the reaction rate constant of acetone with ethanol.¹⁸ They reported 3.7 of $k_{\rm H}/k_{\rm D}$ at room temperature. Our values are close to this value. $k_{\rm H}/k_{\rm D}$ for aliphatic carbonyls may be about this value. Formoshinho et al. made a theoretical calculation of the value of $k_{\rm H}/k_{\rm D}$ for the reactions of acetone with methanol, 2-propanol, and c-C₆. They obtained 3.5, 3.0, 4.0, respectively,¹³ which are very close to the experimental values. As for the temperature dependence no one has examined $k_{\rm H}/k_{\rm D}$ for this reaction experimentally or theoretically.

The isotope effects on the reaction rate constants have been discussed on the basis of the classical transition-state theory. The theory is based on the assumption that thermally activated species determined by a Boltzmann distribution leads to the reaction, and the isotope effect is provided by the difference in the zero-point energies. With the use of the frequencies of the C-H stretching vibrations reported by IR ($\nu_{C-H} = 2900 \text{ cm}^{-1}$ and $\nu_{C-D} = 2050 \text{ cm}^{-1}$), the value of k_H/k_D is estimated to be 7 and 14 at 27 and -43 °C, respectively, if the C-H bond is completely broken in the transition state. $k_{\rm H}/k_{\rm D}$ may become smaller depending on the structure of the transition state. However, the transition-state theory predicts a large temperature dependence on $k_{\rm H}/k_{\rm D}$ and cannot account for our observation that there is little temperature effect on $k_{\rm H}/k_{\rm D}$. On the other hand, the tunneling mechanism has been invoked to interpret the reaction rates that could not be

accounted for by the classical theory. It is thus tempting to try to interpret our results in terms of the tunneling mechanism, particularly because our values are very close to the values calculated by Formoshinho et al.¹³ on the basis of the tunneling mechanism. However, a reliable calculation on the values of $k_{\rm H}/k_{\rm D}$ at various temperatures must be made before we can discuss the reaction mechanism further.

Conclusion

We have examined hydrogen abstraction reactions of carbonyls, especially acetone, with alkanes and 2-propanol using time-resolved EPR and identified several intermediate radicals. We have demonstrated that the dependence of the hydrogen abstraction reaction rates on the position of the hydrogen can be studied by the analyses of the CIDEP spectra. For alkanes we have found that all the secondary hydrogens are abstracted with almost equal rate constants. The relative reactivities for the primary, secondary, and tertiary hydrogens are obtained for acetone and benzophenone to be $k_1/k_3 \le 0.01$ and $k_2/k_3 \simeq 0.1$. This tendency is qualitatively explained by the frontier electron theory based on the simple Hückel MO, but this treatment fails to explain our results on the reactivities among secondary hydrogens. The deuterium isotope effect in the reaction of acetone and cyclopentanone with 2propanol gives $k_{\rm H}/k_{\rm D} \simeq 3-4$ over the temperature range examined (room temperature to -43 °C). This result cannot be explained by the classical transition-state theory.

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Reactions of HS' and S⁻ with Molecular Oxygen, H₂S, HS⁻, and S²⁻: Formation of SO₂⁻, HSSH⁻⁻, HSS⁻²⁻, and HSS⁻

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An electron spin resonance investigation of the reactions of HS' and S' produced from H2S, HS', and S²⁻ in glassy matrices at low temperatures is presented. Co-60 irradiation of 8 M NaClO₄, 12 M LiCl, and alkali-metal hydroxide glasses at 77 K results in the formation of O⁺⁻, Cl₂⁺⁻, and e⁻. Upon annealing to about 150 K O⁺⁻ or Cl₂⁺⁻ reacts with the solutes H₂S, HS⁻, or S²⁻ to form HS[•] and S^{•-} radicals. In the presence of molecular oxygen HS[•] and S^{•-} each react to form sulfur dioxide anion radical, SO2". 17O isotopic studies verify the source of the oxygen in SO2" is the molecular oxygen dissolved in the matrices. In the absence of molecular oxygen, competing processes are clearly observed; i.e., HS* and S** attack H₂S and HS⁻ to form dimer radicals HSSH⁻⁻ and HSS⁺²⁻. At low pH we find that HS⁺ attacks H₂S to form HSS⁺. Mechanisms for the formation of these species are proposed, and hyperfine couplings and g values are reported. Ab initio molecular orbital calculations are performed to aid our understanding of the electronic structure of the various radical species formed and the energetics of their reactions.

Introduction

Extensive studies of thiyl radicals and their reactions have been made because of their biological significance.¹⁻¹⁰ It is well-known

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that thiols are able to donate hydrogen atoms to repair free-radical damage on biomolecules and form more stable thiyl radicals.¹¹⁻¹⁴ Thiyl radicals have been found to form dimer anion radicals, RSSR⁻⁻, through reaction with thiolates and to form perthivl radicals, RSS[•], through reaction with parent thiol.^{5,8,15} Recently, in the presence of molecular oxygen, the formation of sulfoxyl

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