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Study of the Kinetics and Mechanisms of Alkoxy Radical Reactions in the Gas Phase (I). Arrhenius Parameters for *t*-Butoxy Radical Reactions with Isobutane and Cyclohexane

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The relative Arrhenius parameters for *t*-butoxy radical decomposition ($\log A_d, E_d$) and hydrogen abstraction of *t*-butoxy radical from hydrogen donor ($\log A_a, E_a$) by competitive method were obtained as follows: for cyclohexane; $\log A_d/A_a = -4.17$ mole/l and $E_d - E_a = 9.01$ kcal/mole, for isobutane; $\log A_d/A_a = -5.70$ mole/l and $E_d - E_a = 11.0$ kcal/mole. From the reported Arrhenius parameters for *t*-Butoxy radical decomposition reactions the parameters for *t*-Butoxy radical reactions with isobutane and cyclohexane are estimated to be $\log A$ (l/mol·sec) = 8.4, $E_a = 4.3$ kcal/mol and $\log A$ (l/mol·sec) = 9.9, $E_a = 6.3$ kcal/mol, respectively.

1. Introduction

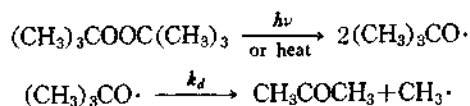
Alkoxy radicals are known to be very important intermediate species in combustion,¹ biological,² and atmospheric chemistry.³ Alkoxy radicals are obtained either by the pyrolyses of peroxides and alkyl nitrites⁴ or by the photolyses of peroxides⁵ and esters.⁶ Alkoxy radicals, once generated, can either decompose to give ketone and alkyl radicals or react with hydrogen donor to give corresponding alcohol. The relative rate constants for the reaction of alkoxy radicals usually determine the distribution of final products.

Most of alkoxy radical reactions have been studied by a competition method. The relative rate constants for the decomposition (k_d) versus hydrogen abstraction reaction (k_a) of alkoxy radicals in liquid phase were extensively studied by Walling and co-workers.^{7,8} The solvent polarity was found to be affecting the activation energies for the decomposition reactions.⁷ Only very recently a direct measurement of absolute rate constant at low temperatures for *t*-butoxy radical reactions with various hydrogen donors by ESR and laser photolysis techniques was reported.^{9,10}

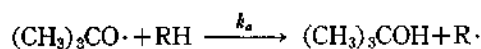
The gas phase decomposition of alkoxy radicals have also been studied by competition method, either with NO reaction,¹¹⁻¹⁴ *i.e.*, $\text{RO}\cdot + \text{NO} \rightarrow \text{RONO}$ vs. $\text{RO}\cdot \rightarrow$ decomposition, or with hydrogen abstraction reaction *i.e.*, $\text{RO}\cdot + \text{R}'\text{H} \rightarrow \text{ROH} + \text{R}'\cdot$ vs. $\text{RO}\cdot \rightarrow$ decomposition. Due to the inaccuracies in the rate constants of reference reac-

tions and the narrow temperature ranges, large discrepancies in Arrhenius parameters have been noticed.^{15,16} Baldwin *et al.* and Batt and coworkers attempted to design a systematic scheme for the estimation of Arrhenius parameters for the alkoxy radical reactions. However, their estimated A factor appears to be too high, so as the activation energies. Recently, Choo and Benson have made a systematic approach on the evaluation of Arrhenius parameters for the alkoxy radical decomposition reactions by a tight transition state model.¹⁷ They showed that the estimated Arrhenius parameters ($\log A = 14.1 \text{ sec}^{-1}$, $E_a = 15.3$ kcal/mole) for *t*-butoxy radical decomposition reactions gave reasonably self-consistent results for the rate constants reported at different laboratories and in different environments.

In this work the ratios of the rate constant of *t*-butoxy radical decomposition versus the rate constant of hydrogen abstraction of *t*-butoxy radical from cyclohexane or isobutane is measured. The basic mechanism of di-*t*-butyl peroxide decomposition is well known,



t-butoxy radicals are decomposed to acetone and methyl radical by β -scission cleavage. When hydrogen donor such as cyclohexane or isobutane is added,



t-butoxy radical abstracts hydrogen from hydrogen donor competitively to the decomposition. Hence the ratio of products (decomposition versus abstraction) distributions in the presence of RH, [acetone]/[*t*-butanol], gives the relative rate constants of each step.

A successful application of the method for the *t*-butoxy radical reaction with trimethylsilane has been reported recently in this laboratory.¹⁸

Usually, the wavelength used in the photolysis of di-*t*-butyl peroxide was mostly 253 nm which is the resonance line of low pressure mercury lamp and a few¹⁹ used 313 nm. It is deemed necessary to check the wavelength dependence of the rate constants ratio by using the super pressure mercury lamp whose output flux is considerably flat in the UV region. It will give some information about the energy state of *t*-butoxy radical and its reaction process.

2. Experiments

A. Apparatus

(1) *Reaction System.* The vacuum line used in this study was a conventional pyrex glass and greaseless high vacuum stop cocks, ACE Glass Co.. A rough vacuum condition, 10^{-2} – 10^{-3} torr, was maintained by a mechanical pump and was monitored by thermocouple gauge, Model 11AH GCA Scientific Co.. High vacuum condition, below 10^{-4} torr, was maintained by operating oil diffusion pump. The ionization gauge, Model RG-830 Veeco Co., showed that vacuum condition of 1×10^{-5} torr could be obtained by evacuating the system for about 5 hours. Before each experiment the vacuum condition was maintained below 1×10^{-3} torr. Electronic pressure gauges, BARATRON sensor gauges, Type 221A series MKS Instruments, Inc., were used for accurate pressure measurement. Two gauges of different pressure ranges were used. Mixing di-*t*-butyl peroxide (DTBP) and cyclohexane or isobutane, various proportions of them were accurately determined by using 0.00–100.00 torr range, MKS 221 AHS-B-100. And when the pressure effect was measured, MKS 221 AHS-B-1000 was used. Reactants were stored in a 1 liter sample reservoir. The sample reservoir was wrapped with aluminium foil to protect the sample from the room light. The reactor was connected to the sample reservoir, to the sampling valve, and to the oil manometer. The sampling valve was connected to the gas chromatograph.

(2) *The Light Source.* The light source was 200 watt super pressure mercury lamp, Baush & Lomb Co. # 33-86-36-01, connected to a DC power supply. The monochromator was combined with mercury lamp house. Its wavelength region is 200–800 nm and its reciprocal dispersion is 6.4 nm/mm. For the photolysis of this reaction system the wavelength region of the light irradiating on the reactor was chosen ± 15 nm from the wavelength selected on the monochromator by adjusting entrance and exit slit width.

(3) *Design of Reactor.* Pyrex tube (18mm I. D. \times 185 mm L.) was connected to the sampling valve, sample reservoir, and oil manometers respectively. Two quartz windows were attached

to the front and the rear of the tube with epoxy resin (Epotek H77, Epoxy Tech. Inc). The vacuum check showed that epoxy resin was suitable to maintain the vacuum of 1×10^{-5} torr. By connecting the transformer between 100 W nichrome wire and temperature controller, Model 4001 KC Omega Co., the temperature of reactor was maintained within $\pm 1^\circ\text{C}$ fluctuation under the input voltage of 20–30 V. A digital thermometer which gives $\pm 0.2^\circ\text{C}$ accuracy was used to read the temperature of the reactor. The volume of reactor was 50.88 ml and the dead volume of the reactor was about 7%.

(4) *Analytical System.* The sample from the reactor goes to the six-port gas sampling valve (Varian Co., injection volume 1 ml) and to the gas chromatograph (Hitachi 154T. TCD detector). We found that Porapak Q combined with DC 200 column was sufficient to separate acetone and *t*-butanol. Using the Porapak Q 10 cm + DC 200 2m column, the optimum GC condition was the following; carrier gas: helium, flow rate; 25 ml/min, oven temperature: 110°C . The absolute quantities of acetone and *t*-butanol formed were measured by the calibrated standard heights of exactly known quantities of acetone and *t*-butanol. When the quantities of acetone and *t*-butanol are smaller than 5 torr in this injection system, peak height of each component was found to be linearly proportional to the peak area.

B. Materials

30 ml of di-*t*-butyl peroxide DTBP, MCB Chemicals, U.S.A., was primarily purified by distillation at 50°C under reduced pressure. Before each experimental step, this was purified by the bulb distillation method. The chromatographic analysis of DTBP showed above 99.5 % purity. Cyclohexane, Merck Co., Spectrograde min. 99.7 %, was used without further purification. Isobutane, Matheson Co. 99.9 %, was used directly from the bottle.

C. Procedure

UV spectra of DTBP and acetone in liquid phase were obtained with Beckmann spectrophotometer, Model 5120.

In the course of main experiments, the wavelength of 280 ± 15 nm was used. Reaction temperatures were selected as 21, 26, 32, 40, 50°C . The ratios of mixtures of cyclohexane versus DTBP were varied in the range of 2–13. At least 5 measurements of *t*-butanol/acetone were done at each temperature. The pressure dependence of *t*-butanol/acetone ratio was checked by adding helium to the mixture of DTBP (3.14 torr) and cyclohexane (15.67 torr). The pressure range of helium added was 0–657.3 torr. The wavelength dependence of *t*-butanol/acetone was again carefully checked using the mixture of DTBP (3.14 torr) and cyclohexane (15.67 torr).

3. Results and Discussion

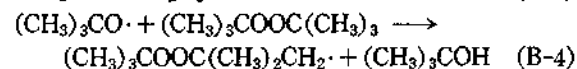
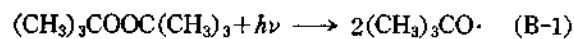
The experimental of various temperatures and various cyclohexane concentrations in the wavelength region 280 ± 15 nm are shown in Table 1. The quantities of acetone and *t*-butanol formed were corrected for the decomposition of acetone by secondary photolysis (Table 3) and for the contribution of di-*t*-butyl peroxide itself to the formation of *t*-butanol (Table 1).

The pressure dependence of *t*-butanol/acetone is shown in

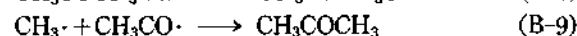
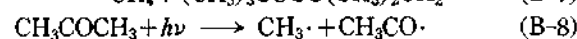
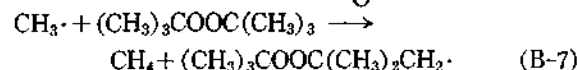
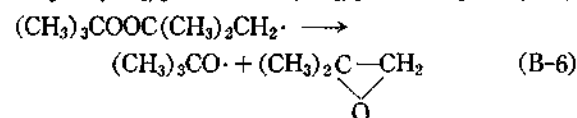
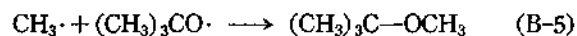
Table 4.

The results of reactions of di-*t*-butyl peroxide-isobutane mixtures at different temperatures and different isobutane concentrations in the wavelength 280 ± 15 nm are shown in Table 5.

The mechanisms accounting for most of the experimental facts in the photolysis of di-*t*-butyl peroxide vapour at temperature below 80° are suggested (or proposed) as follows. The major reactions are²⁰



And the minor reactions are

TABLE 1: Photolysis of DTBP-Cyclohexane Mixture at 280 ± 15 nm

Cyclohexane $\times 10^4$ mole/l	Irrad. time min	Acetone ^b	<i>t</i> -BuOH ^b $\times 10^6$ mole/l	Acetone ^c	<i>t</i> -BuOH ^c	<i>t</i> -BuOH ^c / Acetone
$T=21^\circ\text{C}$						
0	240	10.94	0.81			
0	240	10.14	0.78			
4.29	240	7.11	2.18	7.51	1.40	0.186
7.32	288	8.06	3.66	7.10	2.26	0.316
9.94	240	6.31	3.31	6.67	2.52	0.378
13.75	326	9.62	6.73	7.48	4.17	0.557 ^d
19.50	265	6.31	5.41	6.04	4.11	0.680
$T=26^\circ\text{C}$						
0	240	10.14	0.65			
0	240	10.14	0.71			
4.29	233	8.65	2.38	9.43	1.61	0.171
7.32	258	8.29	3.07	8.17	2.16	0.264
9.94	240	6.97	3.09	7.39	2.40	0.325
13.75	231	6.37	3.34	7.02	2.89	0.412
17.24	240	5.65	5.37	5.99	2.68	0.477 ^d
$T=32^\circ\text{C}$						
0	240	9.97	0.53			
4.29	236	9.85	2.05	10.29	1.55	0.151
7.32	240	7.16	2.13	7.60	1.59	0.209
9.94	240	6.84	2.50	7.25	1.97	0.272
10.71	265	7.92	2.83	7.81	2.03	0.260
17.24	255	7.82	3.68	7.81	2.93	0.376
19.50	308	9.02	4.82	7.45	3.23	0.434
$T=40^\circ\text{C}$						
0	240					
4.29	217	9.40	1.28	11.07	1.00	0.090
10.71	305	10.34	2.74	8.66	1.73	0.200
13.75	235	7.17	2.11	7.80	1.73	0.222
17.24	208	7.48	2.58	9.20	2.56	0.278 ^d
19.50	265	8.05	3.05	7.77	2.34	0.30
$T=50^\circ\text{C}$						
0	240	10.71	0.37			
0	240	10.71	0.31			
7.32	249	8.36	1.06	8.60	0.65	0.076
9.94	193	5.68	0.89	7.54	0.75	0.097
10.71	312	10.58	2.05	8.54	1.20	0.141
13.75	240	7.83	1.79	8.37	1.42	0.170
17.24	227	8.17	2.07	9.22	1.81	0.196 ^d
22.65	281	9.19	2.70	8.39	1.93	0.230

^a Initial quantity of DTBP is 1.72×10^{-4} mole/l (3.14 torr) for each reaction; ^b Apparent quantity detected by GC; ^c Quantities equivalent to 4 hours irradiation and corrected for the contribution of DTBP to the formation of *t*-BuOH and for the decomposition of acetone;

^d Quantity of DTBP is somewhat larger or smaller than average value because of experimental error and of the decrease of the intensity of light source.

TABLE 2: Arrhenius Parameters for DTBP-Cyclohexane and DTBP-Isobutane Mixtures (Per Active C-H Bond)

Mixture	k_a/k_d (l/mole)					E_d-E_a kcal/mole	$\log A_d/A_a$ mole/l
	21°	26°	32°	40°	50°		
DTBP-Isobutane	286	191	162	87.5	51.9	11.0	-5.70
DTBP-Cyclohexane	27.5	21.2	16.3	11.0	6.9	9.01	-4.17

TABLE 3: Quantity of Acetone Decomposed at 280 ± 15 nm

Temp. °C	Initial quantity of acetone $\times 10^5$ mole/l	Irrad. time min	Quantity after photolysis $\times 10^5$ mol/l	Acetone decomposed %
21	3.26	240	2.81	5.4
26				5.6
32				5.8
40				6.1
50	3.06	240	2.76	6.4

TABLE 4: Pressure Dependence of *t*-BuOH/Acetone

Total pressure in reactor torr	Pressure of He added torr	Acetone ^b $\times 10^5$ mole/l	<i>t</i> -BuOH ^b $\times 10^5$ mole/l	<i>t</i> -BuOH ^b /Acetone
18.81	0	4.13	1.67	0.404
32.67	13.86	3.29	1.40	0.426
63.18	44.31	3.41	1.38	0.405
88.03	69.22	3.89	1.54	0.396
297.4	278.6	3.27	1.38	0.422
676.1	657.3	3.39	1.44	0.425

^a Initial quantity of mixture: DTBP; 3.14 torr (1.72×10^{-4} mole/l), Cyclohexane; 15.67 torr (8.58×10^{-4} mole/l); ^b Quantity equivalent to 4 hours irradiation. Used uncorrected values; ^c Quantities of DTBP decomposed are smaller than those in Table 2 because the light intensity of mercury lamp was decreased considerably; ^d $\lambda = 280 \pm 15$ nm, $T = 26^\circ\text{C}$.

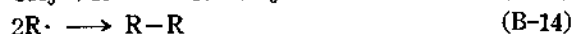
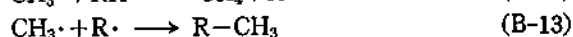
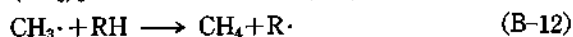
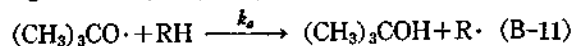
TABLE 5: Photolysis of DTBP-Isobutane Mixture at 280 ± 15 nm

Isobutane $\times 10^4$ mole/l	Temp. °C	Acetone ^b $\times 10^5$ mole/l	<i>t</i> -BuOH ^b $\times 10^5$ mole/l	<i>t</i> -BuOH ^b /Acetone
22.7	21	3.79	2.48	0.654
22.7	26	4.33	1.89	0.436
22.7	32	4.49	1.65	0.367
22.7	40	5.02	1.00	0.199
22.7	50	6.14	0.73	0.119

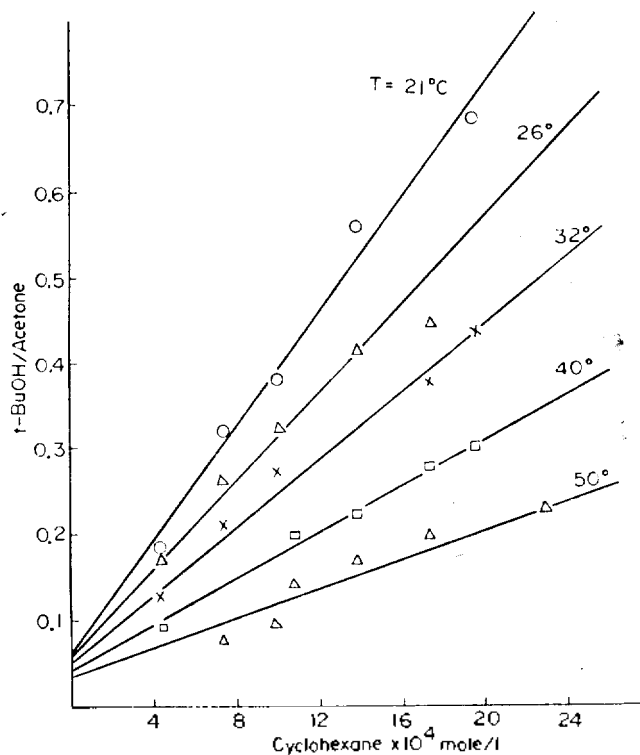
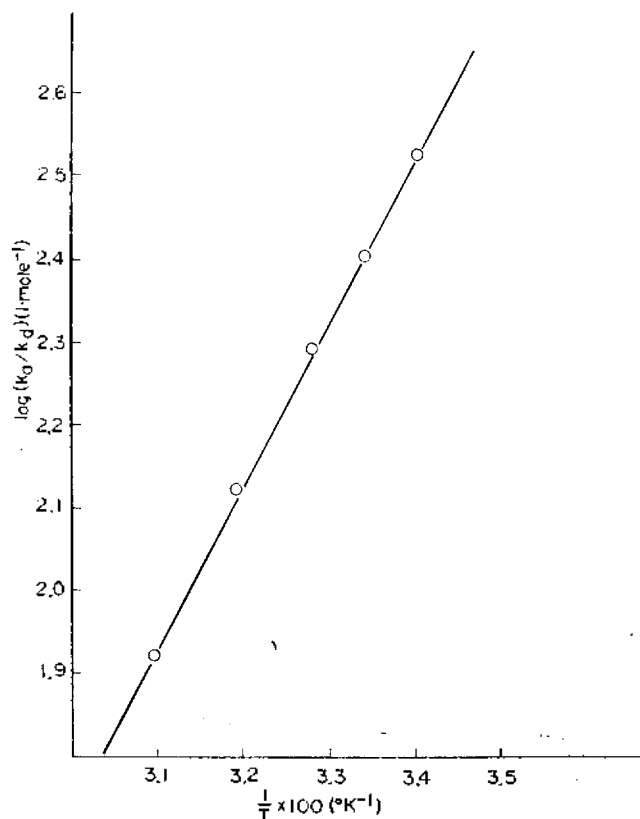
^a Initial quantity of DTBP is 1.72×10^{-4} mole/l (3.14 torr) for each reaction; ^b Quantity equivalent to 4 hours irradiation and corrected for the contribution of DTBP to the formation of *t*-butanol and for acetone decomposition.



When di-*t*-butyl peroxide is decomposed in the presence of hydrogen donor (RH), the possible reactions are



By the steady-state treatment from (B-2), (B-4), (B-8), (B-9), and (B-11) the mechanisms yields the rates of formations of acetone and *t*-butanol as the following,

Figure 1. The plot of $(t\text{-BuOH})/(\text{Acetone})$ for the reaction of DTBP-Cyclohexane Mixture.Figure 2. Arrhenius plot of k_a/k_d for the reaction of DTBP-cyclohexane mixture.

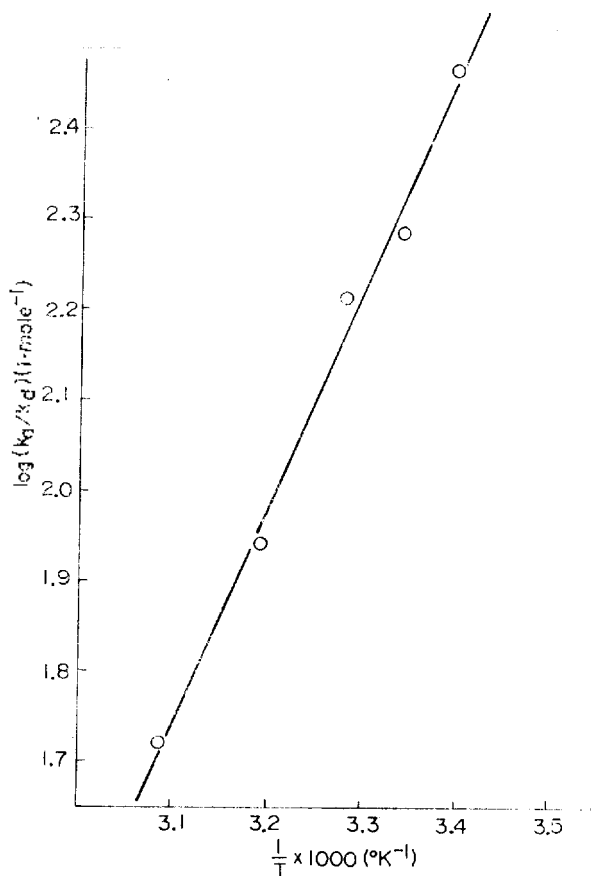


Figure 3. Arrhenius plot of k_a/k_d for DTBP-isobutane mixture.

$$\begin{aligned}
 R_{t\text{-BuOH}} &= \frac{d[t\text{-BuOH}]}{dt} \\
 &= k_4[(\text{CH}_3)_3\text{CO}\cdot][\text{DTBP}] \\
 &\quad + k_2[(\text{CH}_3)_3\text{CO}\cdot][\text{RH}] \\
 [\text{RH}] &: \text{cyclohexane or isobutane} \quad (\text{B-16})
 \end{aligned}$$

and

$$\begin{aligned}
 R_{\text{acetone}} &= \frac{d[\text{acetone}]}{dt} \\
 &= k_d[(\text{CH}_3)_3\text{CO}\cdot] + k_9[\text{CH}_3\cdot] - k_8[\text{acetone}] \quad (\text{B-17})
 \end{aligned}$$

In early stages of reaction,

$$\frac{d[\text{acetone}]}{dt} = k_d[(\text{CH}_3)_3\text{CO}\cdot] \quad (\text{B-18})$$

The ratio of rates of formations of *t*-butanol and acetone becomes

$$\frac{R_{t\text{-BuOH}}}{R_{\text{acetone}}} = \frac{k_4}{k_d}[\text{DTBP}] + \frac{k_2}{k_d}[\text{RH}] \quad (\text{B-19})$$

By subtracting the contribution of *di-t*-butyl peroxide itself to the formation of *t*-butanol, eq(B-20) is obtained.

$$\frac{R_{t\text{-BuOH}}}{R_{\text{acetone}}} = \frac{[t\text{-BuOH}]}{[\text{acetone}]} = \frac{k_2}{k_d}[\text{RH}] \quad (\text{B-20})$$

t-Butanol to acetone ratios for *di-t*-butyl peroxide-cyclohexane mixture at different temperatures and different cyclohexane concentrations are plotted in Figure 1. The ratios of rate constants k_a/k_d found at different temperatures are: 21°C; 329, 26°C; 254, 32°C; 195, 40°C; 132, 50°C; 83, all in units of *l*/mole (Table 2). Arrhenius plot of k_a/k_d is

shown in Figure 2. The slope and intercept yields E_d-E_a of 9.01 kcal/mole and $\log A_a/A_d$ of -4.17 for the reaction of DTBP-cyclohexane mixture. These values are somewhat small compared with the values, E_d-E_a of 10.56 kcal/mole and $\log A_a/A_d$ of -4.61, reported by Walling *et al.*⁸

For DTBP-isobutane mixture the ratios of rate constants, k_a/k_d , at different temperatures are found to be: 21°C; 286, 26°C; 191, 32°C; 161, 40°C; 87.5, 50°C; 51.9, all in units of *l*/mole. The Arrhenius plot of k_a/k_d is shown in Figure 3. The slope and intercept yields E_d-E_a of 11.0 kcal/mole and $\log A_a/A_d$ of -5.70 for DTBP-isobutane mixture. In Table 4, we showed the pressure effect on the $[t\text{-butanol}]/[\text{acetone}]$ ratio. A negligible pressure dependence was noticed in the pressure ranges of 18.8 torr to 676.1 torr.

For the hydrogen abstraction of *t*-butoxy radical from cyclohexane the reference reaction could not be found. From the obtained results for *di-t*-butyl peroxide-cyclohexane mixture and the estimated values of Choo and Benson¹⁷ for the decomposition of *t*-butoxy radical the Arrhenius parameters for hydrogen abstraction of *t*-butoxy radical from cyclohexane are calculated to be $\log A = 9.9 \text{ mole}^{-1} \cdot 1 \cdot \text{sec}^{-1}$ and $E_a = 6.3 \text{ kcal/mole}$ which are in the right range comparing the results of $\log A = 9.1 \text{ mole}^{-1} \cdot 1 \cdot \text{sec}^{-1}$ and $E_a = 6.1 \text{ kcal/mole}$ for the hydrogen abstraction of *t*-butoxy radical from cyclopentane in the liquid phase reported most recently by a direct ESR determination of rate constants.¹⁰ The estimated Arrhenius parameters for the *t*-butoxy radical reaction with isobutane are $\log A = 8.4$ $E_a = 4.3 \text{ kcal/mole}$. Since the major difference in *A* factor between cyclohexane and isobutane is the reaction path degeneracy (12 to 1) it is expected that cyclohexane case should have *A* factor larger than isobutane case by the difference in reaction path degeneracy, $\log A = 1.1$ unit. Comparing with the reported value of $\log A = 8.30 \text{ mole}^{-1} \cdot 1 \cdot \text{sec}^{-1}$ for isobutane case our estimated *A* factor ($\log A = 9.9$) for cyclohexane reaction is in reasonable agreement with the reported *A* factor for isobutane case.

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Synthesis of Nucleophilic Adducts of Thiols (V). Addition of Thioglycolic Acid to ω, ω -Diacetylstyrene Derivatives

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The addition reactions of thioglycolic acid to ω, ω -diacetylstyrene derivatives were investigated. ω, ω -Diacetylstyrene derivatives easily undergo addition reactions with thioglycolic acid to form *s*-[2, 2-diacetyl-1-phenylethyl]-thioglycolic acid, *s*-[2,2-diacetyl-1-(methyl) phenylethyl]-thioglycolic acid, *s*-[2,2-diacetyl-1-(*p*-methoxy) phenylethyl]-thioglycolic acid and *s*-[2, 2-diacetyl-1-(*p*-chloro) phenylethyl]-thioglycolic acid, respectively. The structures of these compounds were identified by neutralization equivalent, UV, IR, and NMR spectral data.

Introduction

The Michael type addition, defined as the nucleophilic addition of an anion to the carbon-carbon double bond of α, β -unsaturated ketone, aldehyde, nitrile, or carboxylic acid derivatives, has been extensively used as an effective method for carbon-carbon bond formation.¹⁻³

The addition of thiols to α, β -unsaturated compounds is interesting because much information has appeared in the literatures⁴⁻⁷ concerning the antiviral and antitumor activities of their adducts.

As a part of the series on the syntheses of nucleophilic adducts of thiols, the addition of cysteine⁸ and thioglycolic acid⁹ to β -nitrostyrene derivatives has been described recently.

We report here our investigation into Michael addition of thioglycolic acid to ω, ω -diacetylstyrene derivatives.

Results and Discussion

The ω, ω -diacetylstyrene derivatives were attempted to

prepare by Kohler's method.¹¹

To a stirred solution of sodium hydroxide in ethanol and water was added benzaldehyde and acetylacetone. After stirring for 2 hours at 20-30°C, the mixture gave yellow precipitate, whose recrystallization from ethanol afforded yellow crystal (I). UV (330nm: *lit.*¹⁰ 282nm), IR (1640cm⁻¹: *lit.*¹⁰ 1690cm⁻¹), NMR (no-COCH₃ peaks) and Mass (MW 234) spectral data revealed that (I) was not ω, ω -diacetylstyrene. (I) was identified as dibenzylideneacetone, C₆H₅-CH=

