Thermal Unimolecular Decomposition of Glyoxal

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The thermal unimolecular decomposition of glyoxal was investigated behind reflected shock waves in the temperature range 1100-1540 K, with argon as a diluent, by monitoring (CHO)2-absorption and CO-emission signals simultaneously. It was ascertained that glyoxal decomposed mainly via channel 1a, $(CHO)_2 \rightarrow 2CO + H_2$, and that the rate of channel 1b, $(CHO)_2$ \rightarrow CH₂O + CO, was relatively low under the present conditions. The reaction took place in the falloff region when total density was changed from 2.8 × 10⁻⁶ to 3.5 × 10⁻⁵ mol cm⁻³. From the theory of unimolecular reaction, the rate constants for the main channel were determined as $k_{\infty} = 10^{14.03} \exp(-55.1 \text{ kcal mol}^{-1}/RT) \text{ s}^{-1}$ in the high-pressure limit and $k_0/[\text{Ar}]$ = $10^{16.41} \exp(-38.4 \text{ kcal mol}^{-1}/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ in the low-pressure limit, respectively. The values of k_{∞} were well connected with the previous data obtained at lower temperatures by using a static method. The fact that channel 1a is more dominant than channel 1b is consistent with ab initio calculations by Osamura et al.⁵

Introduction

The thermal decomposition of glyoxal is considered to occur through the following channels:

> $(CHO)_2 \rightarrow H_2 + 2CO \quad \Delta H_r^{\circ} = 2.5 \text{ kcal mol}^{-1}$ (1a)

 $(CHO)_2 \rightarrow CH_2O + CO \quad \Delta H_r^{\circ}{}_0 = 2.9 \text{ kcal mol}{}^{-1}$ (1b)

$$(CHO)_2 \rightarrow 2CHO \quad \Delta H_r^{\circ}_0 = 77.5 \text{ kcal mol}^{-1} \quad (1c)$$

Figure 1 shows a probable energy diagram for the decomposition of glyoxal. The energy heights for the three channels are the results estimated in this work. In the past, the thermal decomposition of glyoxal was studied below 800 K in static systems.^{1,2} Steacie et al.¹ followed the course of the decomposition of glyoxal by measuring the pressure as a function of time. Although they did not report any rate constants, they found that the reaction was essentially first order with an activation energy of 54 ± 10 kcal mol⁻¹. With more elaborate experiments, Lowden² found that the decomposition proceeded through (1a) and (1b) with a relative ratio of 1.00:5.25, and he evaluated a high-pressure-limit rate constant for the decomposition, $k_{\infty} = 10^{13.14} \exp(-52.6 \text{ kcal})$ mol^{-1}/RT) s⁻¹. According to the photolysis of glyoxal at 313 nm by Calvert and Layne,³ a large part (85%) of the electronically excited glyoxals decomposed to CO and CH₂O and the remainder (15%) decomposed to H_2 and 2CO. Also, the photolysis at 435.8 nm by Parmenter⁴ revealed that the main route of the decomposition was the process to produce CO and CH₂O and that a small amount of H₂ was produced by the route through the vibrationally excited ground state. Thus, most of the previous experiments, involving both pyrolysis and photolysis ($\lambda > 300$ nm), show that the decomposition proceeds via either (1a) or (1b) with no contribution of the single-bond fission (1c). This provides a proper example for the examination of competitive reactions, which are interesting especially in theoretical considerations.

Recently, ab initio calculations were performed for the probable reaction paths corresponding to (1a) and (1b) by Osamura et al.⁵ According to their results, channel 1a is more probable than (1b) in the thermal decomposition in view of energies and geometries of transition states for these channels. It is of interest to ascertain the possibility of channel 1a experimentally, because, to our knowledge, no such concerted reaction has been reported as a unimolecular reaction for relatively small molecules.

In the present work, we followed the disappearance of the shock-heated glyoxal and the production of carbon monoxide

(2) L. F. Lowden, Ph.D. Thesis, University of Oregon, 1972.

simultaneously to clarify the decomposition mechanism.

Experimental Section

The experiments were performed in a shock tube of 9.4-cm i.d., which was pumped by a 6-in. diffusion pump. A detailed description of the equipment was given in a previous paper.⁶ All experiments were performed behind reflected shock waves. The thermal decomposition of glyoxal was monitored by simultaneously observing the visible-light absorption due to the $\tilde{A} \leftarrow \tilde{X}$ transition of glyoxal and IR emission corresponding to the fundamental band of CO. A radiation from a 150-W Xe lamp was used for the absorption experiment, which was passed through a pair of CaF₂ windows mounted on the shock tube walls. The light emerging from the second window passed through an interference filter (474 \pm 5 nm), and it was detected by a photomultiplier (HTV-R106). IR emission from the shock-heated gas was taken out through the first window and was focused on an InSb element at 77 K with a half-silvered mirror and a concave mirror. For the detection of carbon monoxide, in most of the experimental runs, a band-path filter $(4.63 \pm 0.05 \,\mu\text{m})$ was mounted on the entrance window of the detector. These output signals were fed into digital wave memories and were analyzed to obtain kinetic data. The response times of the optical-electrical systems were a few microseconds for the visible absorption and about 10 μ s for the IR emission, respectively. In some experimental runs, IR emission at $3.37 \pm$ 0.13 μ m, which corresponds to CH stretching, was monitored to detect the production of formaldehyde. In an auxiliary experiment, the relative intensities at 3.37 μ m were measured for glyoxal and formaldehyde diluted in Ar. The purpose of this is to investigate the absolute concentration of the formaldehyde produced from the glyoxal pyrolysis.

The glyoxal used in the experiment was prepared as follows. A polymer glyoxal was obtained by dehydration of an aqueous solution ($\sim 40\%$). This polymer was heated together with phosphorus pentoxide to about 150 °C; then a greenish yellow gas, the glyoxal monomer, was generated and trapped at -80 °C. The monomer glyoxal thus obtained was purified by trap-to-trap distillations. During the course of the experiment, the glyoxal was stored as a solid at -80 °C and was only warmed up when a sample of gas was to be withdrawn to prepare a mixture. An IR spectrum of this purified gas showed that there existed no detectable impurities. Formaldehyde, which was used only for the auxiliary experiment, was prepared by heating paraformaldehyde to 120-130 °C and was purified before use.

Prepared gas mixtures (0.1-2.0 mol % in Ar) were stored in glass flasks more than 12 h before use to complete the homogeneous mixing. The experimental conditions behind reflected shock waves were as follows: temperature 1100-1450 K; total density

⁽¹⁾ E. W. R. Steacie, W. H. Hatcher, and J. F. Hoewood, J. Chem. Phys., 3, 291 (1935).

⁽³⁾ J. G. Calvert and G. S. Layne, J. Am. Chem. Soc., 75, 856 (1953).
(4) C. S. Parmenter, J. Chem. Phys., 41, 658 (1964).
(5) Y. Osamura, H. F. Schaefer III, M. Dupuis, and W. A. Lester, Jr., J. Chem. Phys., 75, 5828 (1981).

⁽⁶⁾ K. Saito, T. Yokubo, T. Fuse, H. Tahara, O, Kondo, T. Higashihara, and I. Murakami, Bull. Chem. Soc. Jpn., 52, 3507 (1979).



Figure 1. Schematic potential diagram for the three channels in the thermal decomposition of glyoxal.



Figure 2. Typical profiles of $(CHO)_2$ absorption at 474 nm (upper trace) and CO emission at 4.63 μ m (lower trace). Conditions: T = 1215 K, $[M] = 1.14 \times 10^{-5}$ mol cm⁻³, 2.0 mol % (CHO)₂ in Ar.

 $2.8 \times 10^{-6} - 3.5 \times 10^{-5} \text{ mol cm}^{-3}$.

Results

Glyoxal has an absorption spectrum in the region 390–540 nm for the transition $\tilde{A} \leftarrow \tilde{X}$.⁷ The experiments to determine the absorption coefficient were performed at 474 nm over the temperature and the concentration ranges of the kinetic study. The Lambert-Beer law was ascertained to hold over all experimental conditions, and values of the absorption coefficient (base e) were constant at $(1.8 \pm 0.3) \times 10^4$ cm² mol⁻¹. This value allowed to reduce the absorption records to concentration profiles. Figure 2 shows typical (CHO)₂-absorption and CO-emission signals behind shock waves. The concentration profiles reduced from both signals gave typical exponential curves over the reaction time studied. This did not change with varying the amount of reactant concentration over 20 times, suggesting that the decomposition



Figure 3. Arrhenius plot of k_a at constant total density. [M] = 1.2×10^{-5} mol cm⁻³.

TABLE I: Arrhenius Parameters of ka

total density/ mol cm ⁻³	T/K	A/s ⁻¹	E/kcal mol ⁻¹
2.8×10^{-6}	1140-1385	1.91 × 10 ¹¹	45.8
$5.0 imes 10^{-6}$	1210-1455	4.47×10^{11}	46.8
$1.2 imes 10^{-5}$	1160-1435	6.76×10^{11}	47.0
2.2×10^{-5}	1115-1410	$1.23 imes 10^{12}$	47.9
3.4×10^{-5}	1205-1360	$2.40 imes 10^{12}$	48.6

occurred with a simple mechanism, not with a complex one. Values of the apparent rate constant k_a (first order with respect to the reactant) for the decay of the reactant and for the increase of carbon monoxide were determined from the records of each run. That is, from the (CHO)₂-absorption signals, $k_a = -d[\ln$ $[(CHO)_2]]/dt = -d[\ln (I/I_0)]/dt$, where I_0 and I are the light intensities of 100% transmission and behind reflected shock waves, respectively, and from the CO-emission signals, $I_{ir} \propto [CO]_t \propto$ $[(CHO)_2]_0[1 - exp(-k_a t)]$, where I_{ir} is the emission intensity (arbitrary units) at 4.63 μ m, which was ascertained to be proportional to [CO] by auxiliary experiments for CO-Ar mixtures. Figure 3 shows an Arrhenius plot of k_a for different concentrations of the reactant and for a constant total density, $[M] = 1.2 \times 10^{-5}$ mol cm⁻³. There is no systematic change in the rate constant with the variation of the reactant concentration. In addition, there exists no difference in the rate constants evaluated from the absorption and the emission within experimental error. Thus, the decomposition rate of glyoxal is first order with respect to the reactant over the whole range of the reaction. A straight line drawn in Figure 3 was evaluated by the least-squares fit treatment for the Arrhenius expression of the data. Figure 4 shows a total density dependence of k_a . This figure shows that k_a increases with increasing total density. In Table I, values of the Arrhenius parameters of k_a are listed for each total density. From the behavior of k_a with total density, it is certain that the apparent rate constants are well in the falloff region under the present experimental conditions.

Since the falloff region involves both inter- and intramolecular energy-transfer processes, for the theoretical discussion of each process, it is necessary to evaluate the high- and low-pressure-limit rate constants separately. For this purpose, reduced forms of the

⁽⁷⁾ G. Herzberg, "Molecular Spectra and Molecular Structure", Vol. 3, Van Nostrand, Princeton, NJ, 1967.



Figure 4. Arrhenius plot of k_a for various total densities.

falloff curve were constructed by using the method described in ref 8. Kassel parameters, $S_{\rm K}$ and $B_{\rm K}$,⁹ are as follows. $S_{\rm K} = 6.3$, 6.7, 7.0, 7.3 and $B_{\rm K} = 16$, 16, 15, 15 at 1100, 1200, 1300, and 1400 K, respectively, where the vibrational frequencies of glyoxal were cited from ref 10 and the threshold energy of the decomposition was 52.6 kcal mol⁻¹, which was taken from Lowden's work.² From the lines in Figure 4, rate constants are withdrawn at four selected temperatures and plotted as a function of total density in Figure 5. The reduced falloff curves shown in Figure 5 were fitted to the experimental data points in such a way as to meet the following requirements at the same time: (1) the calculated curves fit the experimental data points reasonably, (2) the high- and low-pressure-limit rate constants give temperature-independent activation energies, $E_{a\infty}$ and E_{a0} , in the experimental region, and (3) the difference between $E_{a\infty}$ and E_{a0} values is represented approximately by the relation $E_{a\infty} - E_{a0} = (S_{eff} +$ 0.5) $R\bar{T}$, where $S_{\text{eff}} = U_{\text{vib}}/R\bar{T}$ and \bar{T} is the mean temperature of the experiments. The rate constants for the high-pressure limit, k_{∞} , and for the low-pressure limit, $k_0/[Ar]$, were then determined in the experimental region as

$$k_{\infty} = 10^{14.03} \exp(-55.1 \text{ kcal mol}^{-1}/RT) \text{ s}^{-1}$$

 $k_0/[\text{Ar}] = 10^{16.41} \exp(-38.4 \text{ kcal mol}^{-1}/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$

In Figure 6, an IR emission record observed at 3.37 μ m is shown. The emission at this wavelength corresponds to the CH stretching in molecules such as glyoxal and products (formaldehyde or formyl radical) if channel 1b or 1c is the case. As seen from Figure 6, the intensity behind the shock front decays exponentially with time. In auxiliary experiments, relative emission intensities at 3.37 μ m were compared between glyoxal and formaldehyde using 0.1 mol % (CHO)₂ in Ar and 0.1 mol % CH₂O in Ar mixtures. It was found from this test that the emission intensities from the two mixtures were essentially equal at the same temperature within experimental scatter.



Figure 5. Falloff curves with temperature as a parameter. Open circles with error bars indicate experimental scatter.



Figure 6. A typical emission profile at 3.37 μ m.

Discussion

Main Reactions of the Glyoxal Pyrolysis. As described in the Introduction, these three channels, (1a)-(1c), are probable as the initial step in the decomposition of glyoxal. The earliest study of this reaction by Steacie et al.¹ suggested that the following reactions occurred to about the same extent together with channel 1a under the conditions of 683-723 K and 30-140 torr.

$$(CHO)_2 \rightarrow C + CO + H_2O$$

$$n(CHO)_2 \rightarrow (CHO)_{2n}$$

However, these channels are omitted from the consideration because the former is unsuitable as an elementary reaction and the latter is neglected in highly diluted mixtures as in the present experiment. Lowden² studied the pyrolysis of glyoxal from 703 to 783 K over a very wide pressure range of 6.3×10^{-4} -51.9 torr

⁽⁸⁾ J. Troe and H. G. Wagner, Ber. Bunsenges. Phys. Chem., 71, 937 (1967).

⁽⁹⁾ J. Troe, Ber. Bunsenges. Phys. Chem., 78, 478 (1974).

⁽¹⁰⁾ A. R. H. Cole and G. A. Osborne, Spectrochim. Acta, Part A, 27A, 2461 (1971).

TABLE II: Reaction Mechanism and Rate Constants

		$log (A/cm^3 mol^{-1} s^{-1})$	$E_{a}/kcal$ mol ⁻¹	
(1a)	$\frac{(\text{CHO})_2 (+\text{M}) \rightarrow}{2\text{CO} + \text{H}_2 (+\text{M})}$	16.8 ^a	47.0	this work
(1b)	$(CHO)_2 (+\dot{M}) \rightarrow CH_2O + CO (+M)$	17.3 ^a	57.7	estimated
(1c)	$(CHO)_2 (+M) \rightarrow 2CHO (+M)$	18.0 ^a	68.2	estimated
(2)	$(CHO)_2 + H \rightarrow CH_2O + CHO$	12.0	0	estimated
(3)	$CH_2O + M \rightarrow CHO + H + M$	15.5	75	ref 12
(4)	$CH_2O + M \rightarrow CO + H_2 + M$	$k_4 < k_3$		ref 12
(5)	$CH_2O + H \rightarrow CHO + H$	13.4	3.8	ref 13
(6)	$CHO + M \rightarrow CO + H + M$	14.2	14.7	ref 11
(7)	$CHO + H \rightarrow CO + H$	14.1	0	ref 11
(8)	$\begin{array}{c} CHO + CHO \rightarrow \\ CH_{2}O + CO \end{array}$	11.0	0	estimated

^a [M] = 1.20×10^{-5} mol cm⁻³.

with a static method. The reaction was followed by the use of a mass spectrometer to determine the partial pressure of the glyoxal in the reaction flask as a function of time. An analysis of the products of the decomposition indicated that the major path was channel 1b and the minor one was channel 1a. And he ascertained that the decomposition was not a free-radical process such as channel 1c. In the present work, we also ascertained that the decomposition rate was first order with respect to the reactant. In addition, there is evidence that channel 1c is not the main route. That is, (1) the experimental activation energy, $E_{a\infty} = 55.1$ kcal mol^{-1} , is much lower than the heat of reaction for (1c), (2) the experimental preexponential factor, $A_{\infty} = 10^{14.03} \text{ s}^{-1}$, is considerably low compared with generally obtained values for the simple bond fission, i.e., $10^{15}-10^{17}$ s⁻¹,¹³ and (3) there is no change in the reaction behavior with changing dilution over 20 times as shown in Figure 3. If channel 1c is the main route, formed CHO radicals decompose rapidly to CO and H, then the decomposition of glyoxal should be governed by a chain mechanism involving H atoms as in the case of formaldehyde.^{11,12} However, such a chain behavior could not be observed in this experiment. Thus, channel 1c does not contribute significantly to the decomposition of glyoxal under the present experimental conditions, being consistent with the Lowden's work.

As described in the results, the emission intensity at 3.37 μ m corresponds to the decomposition of glyoxal rather than to the formation of formaldehyde. That is, in Figure 6, the intensity decays exponentially with time toward almost zero level and does not reveal any production of stable CH compounds within the reaction time ($\sim 10^{-3}$ s). If channel 1b is the important route, the emission profile at 3.37 μ m should be affected by the formaldehyde produced because the emission intensity of formaldehyde is nearly equal to that of glyoxal as stated above. Also, it was ascertained that apparently formaldehyde did not decompose within 10⁻³ s under the experimental conditions considered here.^{11,12} From these facts, it appears that the amount of formaldehyde produced by the decomposition is too small to be detected. This is in contrast to Lowden's mechanism. A possible reason, but not conclusive, for this serious discrepancy is as follows. In Lowden's work, the reaction mechanism was determined by analyzing the product after the reaction. There are some problems regarding



Figure 7. Calculated concentration profiles of each species. Conditions are same as those in Figure 2.

the measurement of the relative concentration of each product from a mass spectrum. Since there still remains a fraction of the reactant at the end of the reaction time, it affects the mass peak heights of each product.

As an overall thermal decomposition of glyoxal in the present system, ten elementary reactions were considered to be important, which are listed in Table II together with rate constants. With use of this mechanism, a computer simulation was performed to check whether the overall reaction is essentially governed by channel 1a as the results obtained in this experiment. Values of the rate constants for (1b) and (1c) were estimated in this work as will be discussed later. The other rate constants were cited from the literature listed or assumed based on the data for similar reactions. A calculated result under typical experimental conditions is shown in Figure 7. From Figure 7, it is certain that the decomposition of glyoxal produces mainly carbon monoxide and the hydrogen molecule via channel 1a and that the production of formaldehyde is less than one-tenth of the reduction of the reactant.

Low-Pressure-Limit Rate Constants. The rate constant in a low-pressure region reflects the behavior of the intermolecular energy transfer in collisions between reactant and diluent. Experimentally, the low-pressure-limit rate constant is available directly from small molecules diluted in rare gases at relatively high temperatures. The importance of the weak-collision effects arises from the fact that the collisional energy transfer becomes inefficient at high temperatures.¹⁴ These effects are evaluated from the difference between the observed low-pressure rate constant and the strong-collision rate constant. Since it is very difficult to obtain the strong-collision rate constant experimentally, especially at high temperatures, generally the rate constant is evaluated from a theoretical expression. A convenient equation for the strong-collision rate constant of a thermal unimolecular reaction was proposed by Troe.¹⁵

$$k_0^{\text{SC}} = [M] Z_{\text{LJ}} \int_{E_0}^{\infty} Q^{-1} \rho(E) \exp(-E/RT) dE$$

where Z_{LJ} is the Lennard-Jones collision frequency, E_0 the threshold energy of the reaction, $\rho(E)$ the density of states at E, and Q the partition function of the reactant. The integral term in the above equation has been expressed in factorized form in

⁽¹¹⁾ A. M. Dean, B. L. Craig, R. L. Hohnson, M. C. Shultz, and E. E. Wang, Symp. (Int. Combust., [Proc.], 17, 1978, 577 (1979).

⁽¹²⁾ K. Saito et al., to be submitted for publication. The thermal decomposition of CH₂O was investigated for mixtures containing from 10 to 10⁴ ppm in Ar.

⁽¹³⁾ S. W. Benson, "Thermochemical Kinetics", 2nd ed., Wiley, New York, 1976, Chapter 3.

⁽¹⁴⁾ J. Troe and H. G. Wagner, Ber. Bunsenges. Phys. Chem., 71, 967 (1967)

⁽¹⁵⁾ J. Troe, J. Chem. Phys., 66, 4745, 4858 (1977).

TABLE III: Calculated Parameters for Low-Pressure-Limit Rate Constant of Channel 1a^a

	$10^{-14} Z_{L,J}/cm^3$					$(k_0^{\rm sc}/[{\rm Ar}])/$		$-\langle \Delta E \rangle /$
T/K	$mol^{-1} s^{-1}$	F_E	$F_{\rm rot}$	$F_{ m rot,int}$	$Q_{\rm vib}$	cm ³ mol ⁻¹ s ⁻¹	β_{c}	kcal mol ⁻¹
1100	2.98	1.38	2.87	2.91	28.8	1.14×10^{10}	0.052	0.20
1200	3.05	1.43	2.67	2.69	42.9	6.21×10^{10}	0.041	0.18
1300	3.13	1.48	2.50	2.49	63.5	2.48×10^{11}	0.036	0.17
1400	3.20	1.53	2.35	2.33	93.2	7.75×10^{11}	0.033	0.17

 ${}^{a}E_{0} = 55.1 \text{ kcal mol}^{-1}; E_{z} = 22.5 \text{ kcal mol}^{-1}; \sigma_{LJ}^{Ar} = 3.542 \text{ Å}; \sigma_{LJ}^{(CHO)_{2}} = 4.739 \text{ Å}; \epsilon_{LJ}^{Ar} = 93.3 \text{ K}; \epsilon_{LJ}^{(CHO)_{2}} = 428.3 \text{ K}; M^{Ar} = 39.948 \text{ g mol}^{-1}; M^{(CHO)_{2}} = 58.037 \text{ g mol}^{-1}; \rho_{\text{vib},\text{h}} = 2.41 \times 10^{6} \text{ mol kcal}^{-1} \text{ (without torsion)}; a(E_{0}) = 0.935; F_{\text{anh}} = 1.59 \text{ (σ and ϵ for glyoxal were evaluated from ref 24)}. Explanation of each symbol is given in ref 15.}$

TABLE IV: Strong- and Weak-Collision Rate Constants for (1b) and (1c)

reacn 1b ^a			reacn 1c ^b		
T/K	$\frac{(k_0^{\text{sc}}/[\text{Ar}])}{\text{cm}^3 \text{ mol}^{-1} \text{ s}^{-1}}$	$\frac{(k_v/[Ar])}{cm^3 mol^{-1} s^{-1}}$	$\frac{(k_0^{\text{sc}}/[\text{Ar}])}{\text{cm}^3 \text{ mol}^{-1} \text{ s}^{-1}}$	$\frac{(k_{\rm o}/[{\rm Ar}])}{{\rm cm}^3 {\rm mol}^{-1} {\rm s}^{-1}}$	
1100 1200 1300 1400	$\begin{array}{c} 2.83 \times 10^8 \\ 2.35 \times 10^9 \\ 1.33 \times 10^{10} \\ 5.62 \times 10^{10} \end{array}$	$\begin{array}{c} 1.47 \times 10^{7} \\ 9.66 \times 10^{7} \\ 4.72 \times 10^{8} \\ 1.84 \times 10^{9} \end{array}$	$\begin{array}{c} 1.11 \times 10^{7} \\ 1.37 \times 10^{8} \\ 1.08 \times 10^{9} \\ 6.02 \times 10^{9} \end{array}$	$5.75 \times 10^{5} 5.63 \times 10^{6} 3.83 \times 10^{7} 1.97 \times 10^{8}$	
a_{E_0}	$= 66 \text{ kcal mol}^{-1}$	$^{b}E_{0} = 77.5$ k	cal mol ⁻¹ .		

ref 15 in order to facilitate the calculation. A calculated result for channel 1a is listed in Table III. The molecular constants used in the calculation are shown in the footnote of Table III. The calculation of the strong-collision rate constant and the comparison with the experimental value lead to the empirical weak-collision efficiency $\beta_c = k_0/k_0^{SC}$, which summarizes all weak-collision effects. Also, the average energy transferred in a collision, $\langle \Delta E \rangle$, is approximately related to β_c as¹⁵

$\beta_{\rm c}/(1-(\beta_{\rm c})^{1/2})\approx -\langle\Delta E\rangle/F_E RT$

Values of β_c and $-\langle \Delta E \rangle$ are also listed in Table III. The evaluated $-\langle \Delta E \rangle$ value, 0.17 kcal mol⁻¹, is considered to be reasonable compared with the data for the other molecule-Ar systems, for example, 0.15 kcal mol⁻¹ at 1900 K for methyl chloride,¹⁶ 0.09 kcal mol⁻¹ at 1100 K for methyl iodide,¹⁷ and 0.12 kcal mol⁻¹ at 1100 K for trifluoroiodomethane.¹⁸ $-\langle \Delta E \rangle$ becomes higher for larger molecules, e.g., 0.72 kcal mol⁻¹ for cycloheptatrienes (including methyl- and ethyl-substituted ones).¹⁹ The temperature dependence of $-\langle \Delta E \rangle$ in the present system is nearly T⁰ (strictly speaking, it decreases very slightly with temperature), being consistent with the theoretical expression.¹⁵

The above relation between k_0 and k_0^{SC} may be applied to the calculation of unknown rate constants at the low-pressure-limit by using the evaluated $\langle \Delta E \rangle$ value. Thus, calculations were performed for the other channels, (1b) and (1c), with the same procedure described above. The results are shown in Table IV. In the calculations, the threshold energy E_0 for (1b) was given a value of 66 kcal mol⁻¹, which was estimated from the potential energy ratio, V(1b)/V(1a) = 1.2, obtained from ref 5. On the other hand, for (1c), $\Delta H_r^{\circ}{}_0 = 77.5$ kcal mol⁻¹ was used as E_0 . Consequently, low-pressure-limit rate constants for (1b) and (1c) were expressed as

 $k_0^{1b}/[Ar] = 10^{16.95} \exp(-49.2 \text{ kcal mol}^{-1}/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and

 $k_0^{1c}/[Ar] = 10^{17.60} \exp(-59.6 \text{ kcal mol}^{-1}/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$

respectively. These are shown in Figure 8 to compare with $k_0^{1\bar{a}}/[\mathrm{Ar}].$

High-Pressure-Limit Rate Constants. Figure 9 shows highpressure-limit rate constants for the glyoxal decomposition obtained in this work and in Lowden's work. Since Lowden monitored the



Figure 8. Comparison of low-pressure-limit rate constants for the three channels.



Figure 9. Arrhenius plot of the high-pressure-limit rate constants for the thermal decomposition of glyoxal.

glyoxal concentration as a function of time, the rate constants determined correspond to the disappearance rate of the reactant, although he concluded that channel 1b was dominant in the decomposition on the basis of the product analysis. It appears

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(19) D. C. Astholz, J. Troe, and W. Wieters, J. Chem. Phys., 70, 5107</sup> (1979).



Figure 10. Schematic explanation of the photodissociation routes.

from Figure 9 that these two results evaluated in different temperature regions are well connected with a straight line (as shown by a dotted line), although the Arrhenius parameters in each work are slightly different (in Lowden's work, $A = 10^{13.14} \text{ s}^{-1}$ and $E_a = 52.6 \text{ kcal mol}^{-1}$). Thus, so far as the overall decomposition of glyoxal is concerned, these experimental results are in close agreement with each other, regardless of different experimental methods.

Recently, ab initio calculations have been performed for several unimolecular reactions.²⁰ Schaefer and his co-workers^{5,21} paid attention to the interesting channels in the photodissociation of glyoxal⁴ and tried to calculate probable transition states to examine especially the possibility of the concerted reaction, i.e., channel 1a. Their calculated results are of great interest, which provide valuable information when experimental results are examined. Thus, we tried to evaluate rate constants by using the calculated results on the basis of the transition-state theory. In the calculations, they used four different basis sets. However, there was no serious difference in the geometries of the probable transition states obtained with these basis sets. As the 3-21G basis set was used for both channels considered here, we used the data calculated with this basis set for the purpose of the comparison between the

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preexponential factors for the two channels. Calculated A factors are $10^{14.1}$ s⁻¹ for (1a) and $10^{13.7}$ s⁻¹ for (1b), respectively, at 1300 K, where $A = (kT/h)(Q^*/Q)$. In the calculation of the partition function, Q, for glyoxal, both trans and cis forms were considered. Considering the differences in the A factors and in the calculated (ab initio) potential energies for the transition states (81.2 kcal mol⁻¹ for (1a) and 102.3 kcal mol⁻¹ for (1b)),⁵ it is suggested that the rate of (1a) is much faster than that of (1b). This is consistent with the present experimental results, and, encouragingly, the value of $A = 10^{14.1}$ s⁻¹ for (1a) is in close agreement with the experimental value.

Comparison with the Photodecomposition. It is important to compare the results of the thermal decomposition and the photodecomposition in order to discuss the reaction path. There have been reported many experimental results for photochemical processes in glyoxal since the early study by Norrish and Griffiths using a mercury arc light.²² Product analyses in some experiments show that formaldehyde and carbon monoxide are the main products of the photolysis; on the other hand, the hydrogen molecule is only a minor product,^{3,4} The route of the photodecomposition using wavelengths longer than ca. 300 nm has been considered as shown in Figure 10.^{4,5,23} That is, the excited \tilde{A}^1A_u state molecules transfer to the \tilde{a}^3A_u state via path II, and a decomposition occurs to produce CH₂O and CO, path III. In part, the vibrationally excited ground state is formed by intersystem crossing from the a state, path IV, and dissociates to H₂ and 2CO via path V, i.e., channel 1a. Since the threshold energy, $E_0 = 55.1$ kcal mol⁻¹, for channel 1a is close to the lowest ã state, 54.9 kcal mol⁻¹, the population of the vibrationally excited $\tilde{\mathbf{X}}$ state above E_0 is very low due to the rapid vibrational relaxation. This is the reason for the small amount of H₂ production in the photodissociation. In the thermal reaction, vice versa, most of the molecules that are thermally excited above E_0 decompose to H₂ and 2CO via path V before they transfer to the a state. In this sense, the result that the E_0 value is close to the lowest \tilde{a} state is thought to be very reasonable to explain the experimental results involving both the thermal and the photodissociation studies.

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First Electron Spin Resonance Identification of a Nitrogen Peroxy Radical as Intermediate in the Photooxidation of 2,2,6,6-Tetramethylpiperidine Derivatives

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ESR evidence has been obtained for the existence of an N-peroxyl radical intermediate in the conversion of the 2,2,6,6tetramethylpiperidinaminyl radical to the corresponding nitroxide. This observation is of interest for the understanding of the mechanism of photostabilization of polyolefines by tetramethylpiperidine derivatives. The species identified is the first example of a novel class of peroxy radicals characterized by the direct binding of the oxygen atoms to a nitrogen atom; information regarding its structure has been obtained by INDO MO calculations and by ¹⁷O ESR measurements.

The inhibition mechanism of polypropylene photooxidation by 2,2,6,6-tetramethylpiperidine (TMP) derivatives has been the

object of numerous investigations¹ but several important aspects of the mechanism are still far from being fully understood. A