

will be of value in studying singlet oxygen interactions in 100% aqueous systems, where 1,3-diphenylisobenzofuran cannot be used because of insolubility and dimerization problems.<sup>5</sup>

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## Quenching by Hydrogen Bromide of the Norrish Type II Process in the Photolysis of 2-Pentanone. Chemical Trapping of a Triplet 1,4 Biradical in the Gas Phase

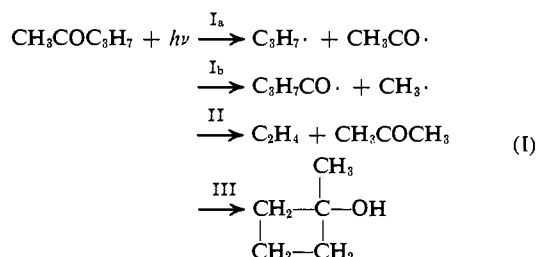
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**Abstract:** The effect of hydrogen bromide on the gas phase 2-pentanone photochemistry (3130 Å, 35–194°) is reported. The Norrish type II primary process (intramolecular elimination to ethene and acetone) and the Norrish type I process (simple bond fission) are both significantly reduced by hydrogen bromide. The dominant type I process is shown to be reaction to acetyl and *n*-propyl radicals. Quenching by HBr is explained in terms of chemical trapping of the 2-pentanone 2,5-triplet biradical intermediate ( $T_R$ ) formed *via* the six-center intramolecular H-abstraction reaction which is known to precede type II product formation in the uninhibited system. A lifetime for  $T_R$  of  $10^{-4.9}$  sec at the mean reaction temperature (388°K) is calculated from the data. An extended primary process mechanism involving singlet and triplet biradical states as well as singlet and triplet ketone states is proposed. Available data are shown to be consistent with the mechanism and are used to obtain reasonable rate constant and rate constant ratio values. An estimate of the equilibrium constant for the singlet to triplet biradical exchange reaction of  $K_{S_R \rightarrow T_R} = 1.1 \times 10^8$  (25°) is deduced. Relevance of the rate constants obtained for spin inversion between triplet and singlet biradicals to recent interpretations of spin correlation effects is discussed.

The photolysis of 2-pentanone is a complex and interesting system since, as shown below, three different primary processes are known to occur: Norrish type I, simple bond fission; Norrish type II, intramolecular elimination; and isomerization to a cyclobutanol derivative (designated here as process III).

2-Pentanone primary processes



A wealth of quantum yield data exists for all three primary processes over a range of experimental variables ( $T$ ,  $\lambda$ , and  $P$ ) in both the gas phase and in solution.<sup>1-7</sup> The influence of various triplet state quenchers on the primary process quantum yields has also been rather extensively investigated.

(1) F. S. Wettack and W. A. Noyes, Jr., *J. Amer. Chem. Soc.*, **90**, 3901 (1968).

(2) J. L. Michael and W. A. Noyes, Jr., *J. Amer. Chem. Soc.*, **85**, 1027 (1963).

(3) P. J. Wagner and G. S. Hammond, *J. Amer. Chem. Soc.*, **87**, 4009 (1965).

(4) N. C. Yang, S. P. Elliott, and B. Kim, *J. Amer. Chem. Soc.*, **91**, 7551 (1969); N. C. Yang and S. P. Elliott, *ibid.*, **91**, 7550 (1969).

(5) Peter J. Wagner, *Accounts Chem. Res.*, **4**, 108 (1971).

(6) J. G. Calvert and C. H. Nicol, *J. Amer. Chem. Soc.*, **89**, 1790 (1967).

(7) P. Ausloos and R. E. Rebert, *J. Amer. Chem. Soc.*, **83**, 4897 (1961).

The most important of these observations, including those of the present study, are summarized and referenced in Table I. Although the many observations on this system have prompted numerous interpretations dealing with specific aspects of mechanism, no detailed mechanistic scheme addressing and correlating data on all three processes has ever been presented.

With the modest intention of obtaining gas phase kinetic parameters for the type II process (*i.e.*,  $A_{II}$  and  $E_{II}$ ) originating from the 2-P triplet state and of determining the lifetime of that state, we investigated the 2-P photochemistry at 3130-Å exciting radiation in the presence of varied amounts of hydrogen bromide over the temperature range 35–194°. Since prior results indicated that most of the type II process occurred *via* the triplet state of 2-P,<sup>1-5</sup> and since hydrogen bromide has been demonstrated to be a very efficient trapping agent for the acetone triplet,<sup>8</sup> it seemed reasonable that a study of the temperature dependence of the type II quenching effected by HBr would lead to the desired information. As anticipated, type II quenching was observed; however, the nature of the quenching process was not as expected. Our results indicate that in addition to upper singlet and triplet ketone states both singlet and triplet 1,4 biradicals are very important photochemical reaction intermediates and that hydrogen bromide quenches the type II reaction by trapping the triplet biradical and not the triplet ketone.

We have correlated our HBr-quenching data with the existing wealth of quantum yield data for the 2-P photochemical system and propose here a compre-

(8) C. W. Larson and H. E. O'Neal, *J. Phys. Chem.*, **70**, 2475 (1966).

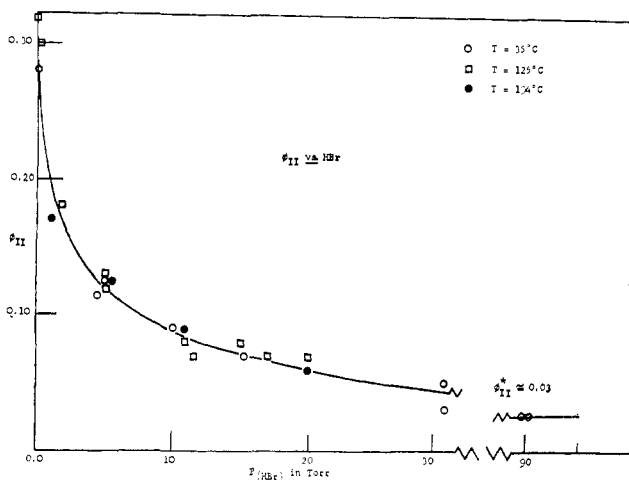


Figure 1. Effect of hydrogen bromide on type II quantum yields of 2-pentanone.

hensive mechanism for the reaction. The essential features of the mechanism are shown to be consistent with most of the available data. Unfortunately, the data are not sufficiently complete to resolve all the problems of mechanism. Interesting alternatives for interpretations of some of the observations are presented. The most reasonable of these have been selected and rate constant estimates made accordingly. However, the final test of mechanism and evaluation of rate constants must await experimental data on the primary process reactions still in question.

### Experimental Procedures and Results

The experimental apparatus and procedures employed were described in detail for a prior study.<sup>8</sup> The essential features worth noting again are: the light source was an air-cooled Osram 200-W high-pressure mercury arc; wavelengths in the 3130-Å region were isolated using a 10-cm path length nickel-cobalt sulfate-1-cm path length potassium biphthalate filter combination; 3-pentanone was employed as an external actinometer fluid; toluene was added to the system to maintain hydrogen bromide concentrations at a constant level *via* the regeneration reaction  $\text{Br} + \text{PhCH}_3 \rightarrow \text{HBr} + \text{PhCH}_2\cdot$ ; 2-pentanone pressures were always approximately 20 Torr; and condensation of both reactants and products in the presence of hydrogen bromide was scrupulously avoided. The reaction cell was loaded by expanding the higher pressure gaseous reactants into the reaction cell filled in prior operations by the lower pressure reactants, and hydrogen bromide was removed from the gaseous products by passing the product mixture through auramine which reacts with it to form an immine salt.

Quantum yield data are shown in Table II. It is apparent from the striking reductions in the ethylene quantum yields for systems with added hydrogen bromide (Figure 1) that the latter is a very efficient quenching agent for the type II reaction. Similar reductions in methane, propane, and carbon monoxide quantum yields show that the type I process is also significantly quenched by hydrogen bromide, particularly at the higher two temperatures.

**Mechanism.** To explain the results and correlate them with other data presently available in the litera-

Table I. Experimental Observations for 2-Pentanone Photolysis

Type I Process	
(1)	$\Phi_1$ yields are $T$ independent above 125°. <sup>a</sup> 3130 Å: $\Phi_1 = \Phi_{\text{CO}} = 0.40 \pm 0.05$ (gas phase)
(2)	$\Phi_1$ yields are strongly reduced by HBr: <sup>a</sup> $\Phi_1$ (excess HBr) $\approx 0.10$
(3)	$\Phi_1$ yields appear to increase with $T$ between 25 and 125° (see text)
Type II Process	
(1)	$\Phi_{11}$ is $T$ , $\lambda$ , and $P$ independent <sup>1,6,7</sup> 3130 Å: $\Phi_{11} \approx 0.28 \pm 0.03$ (gas phase) $\approx 0.30$ (solution) <sup>3,7</sup> 2537 Å: $\Phi_{11} \approx 0.34$ (gas phase) <sup>1</sup>
(2)	$\Phi_{11}$ yields are quenched by triplet ketone quenching agents 3130 Å (excess 1,3 dienes): $\Phi_{11} \approx 0.11^1$ (gas phase) (excess biacetyl): $\Phi_{11} \approx 0.11^2$ (gas phase) (excess 1,3-pentadiene): $\Phi_{11} \approx 0.04^3$ (solution)
(3)	$\Phi_{11}$ yields are quenched by $T_R$ quenching agents 3130 Å (excess HBr): $\Phi_{11} \approx 0.03^a$
Process III	
(1)	$\Phi_{111}$ yields increase with increasing pressure (gas phase) 3130 Å ( $T = 25^\circ$ ): $\Phi_{111} = 0.027$ (1.3 Torr) <sup>7</sup> $= 0.106$ (32 Torr) <sup>7</sup>
(2)	$\Phi_{111}$ yields in the gas phase decrease with increasing temperature and decreasing wavelength 3130 Å (15 Torr): $\Phi_{111} = 0.063$ (25°): $\Phi_{111} = 0.036$ (150°) <sup>7</sup> 2537 Å (15 Torr): $\Phi_{111} = 0.028^7$
(3)	$\Phi_{111}$ yields are temperature and wavelength independent in solution 3130 Å and 2537 Å: $\Phi_{111}/\Phi_{11} = 0.45 \pm 0.03^7$
(4)	$\Phi_{111}$ yields are reduced by triplet ketone quenching agents to a greater degree than are $\Phi_{11}$ yields gas phase: $\Phi_{111}/\Phi_{11} = 0.252$ no additive <sup>7</sup> $= 0.107$ 9.8 cm O <sub>2</sub> solution: $\Phi_{111}/\Phi_{11} = 0.45$ no additive $= 0.07$ 1,3-pentadiene excess
General Observations	
(1)	Fluorescence from ${}^1K$ is very small but is enhanced by increasing pressure at all wavelengths. At 3130 Å, pressure enhances fluorescence up to pressures of 200-300 Torr <sup>1</sup>
(2)	Total quantum yields ( $\Phi_1 + \Phi_{11} + \Phi_{111}$ ) are significantly less than unity. <sup>1</sup> Solution studies of racemization of optically active ketones at the $\gamma$ -carbon position show that $\Phi_{\text{rac}}$ is large and closely equal to $1 - (\Phi_1 + \Phi_{11} + \Phi_{111})$ . <sup>5</sup> Hence return to the ground state ketone (nonradiative decay) involves chemical processes, specifically the inverse of the type II intramolecular H abstraction

<sup>a</sup> This study.

ture, we propose the mechanism of Scheme I. The energetics shown represent our best estimates generated from available thermodynamic data.<sup>9</sup> Details of this mechanism and support for the various steps shown are discussed and presented in the following sections.

**Type II Process.** As shown in Figure 1, ethylene quantum yields are appreciably reduced by hydrogen bromide at all three reaction temperatures (35, 125, and 194°) and  $\Phi_{\text{C}_2\text{H}_4} = \Phi_{\text{II}}$ . Features to note are: (1) the quenching is temperature independent within experimental error; (2) the quenching approaches a limiting value of  $\Phi_{\text{II}}^* \approx 0.03$  at "high" HBr pressures. Unfortunately, we have been unable to identify the product of the hydrogen bromide trapping reaction. A reduction to 2-pentanol seems most probable; how-

(9) H. E. O'Neal and S. W. Benson, *J. Phys. Chem.*, **71**, 2903 (1967); S. W. Benson and H. E. O'Neal, *Nat. Stand. Ref. Data Ser., Nat. Bur. Stand.*, No. 21 (1970); S. W. Benson, "Thermochemical Kinetics," Wiley, New York, N. Y., 1968; H. E. O'Neal and S. W. Benson, "Free Radicals," Vol. II, J. K. Kochi, Ed., Wiley, New York, N. Y., 1973.

Table II. Product Quantum Yields (2-Pentanone, 3130 Å, Torr)<sup>a</sup>

$P_{\text{HBr}}$ , Torr	Product quantum yields						Type II $\text{C}_2\text{H}_4$	Type I $\Phi_1$
	CO	$\text{CH}_4$	$\text{C}_2\text{H}_6$	$\text{C}_3\text{H}_8$	$\text{C}_3\text{H}_6$	$\text{C}_4\text{H}_{10}$		
$T = 35^\circ$								
0	0.19	0.06	0.02	0.09		0.01	0.28	>0.19
0	0.14	0.07	0.01	0.09		0.01	0.23	>0.14
4.5	0.02	0.04		0.08		0.02	0.113	0.14
5.0	0.01	0.01		0.10		0.01	0.125	0.12
10.0	0.09 <sup>b</sup>	0.08 <sup>b</sup>	0.01	0.09		0.01	0.089	0.11
15.3	0.02	0.01	0.00	0.08			0.070	0.08
30.0	0.02			0.10			0.048	0.10
30.3	0.01			0.12			0.030	
89				0.11			0.026	
93				0.11			0.026	
$T = 125^\circ$								
0	0.40	0.05	0.04	0.17	0.01	0.10	0.32	0.40
0	0.43	0.17	0.09	0.16	0.02	0.25	0.39	0.43
0	0.45	0.24	0.06	0.11	0.02	0.08	0.30	0.45
1.8	0.24	0.24	0.03	0.29		0.02	0.18	>0.29
5.0	0.05	0.04	0.05	0.20		0.01	0.13	0.20
5.2	0.03			0.19			0.12	0.19
11.0	0.01	0.02	0.02	0.11			0.08	0.11
11.5	0.02	0.01	0.02	0.15			0.07	0.15
15.0				0.10			0.08	0.10
17.5	0.03	0.01	0.01	0.10			0.07	0.10
20.0	0.03	0.01	0.01	0.10			0.07	0.10
$T = 194^\circ$								
0	0.35	0.24	0.01	0.17	0.04	0.02	0.28 <sup>c</sup>	0.35
0	0.43	0.20	0.01	0.19	0.05	0.03	0.28 <sup>c</sup>	0.43
1.0	0.36	0.27	0.02	0.22	0.02	0.02	0.17	0.36
5.0	0.18	0.14	0.02	0.19		0.02	0.13	0.19
11.0	0.03	0.03	0.01	0.14			0.09	0.14
20.0	0.03	0.01	0.01	0.10			0.06	0.10

<sup>a</sup> 2-Pentanone pressures = 20 Torr. <sup>b</sup> Clearly erroneous values. <sup>c</sup> Assumed values.

ever, quantitative analysis of the condensable reaction products was complicated by the occurrence of dark reactions. These did not, however, form any of the gaseous products which were the prime monitors of the type I and II reactions.

A Stern-Volmer plot of the function  $(\Phi_{\text{II}}^0 - \Phi_{\text{II}}^*)/(\Phi_{\text{II}} - \Phi_{\text{II}}^*)$  vs.  $P_{\text{HBr}}$  provides a measure of the effect of hydrogen bromide on type II yields which are able to be reduced by hydrogen bromide. The slope of such a plot is generally equated to the product of the natural lifetime of the quenched state ( $^X\tau$ ), where the superscript X refers to the identity of the quenched state and the rate constant of the quenching reaction ( $k_{\text{T}}$ ). This identification, which is close but not entirely correct in our system (see later), gives

$$k_{\text{T}}^X\tau = 0.33 \text{ Torr}^{-1} = 8.0 \times 10^3 \text{ l./mol} \quad (\text{II})$$

$$\bar{T} \text{ (mean } T \text{ of experiments)} = 388^\circ\text{K}$$

That the type II process occurs *via* a consecutive step mechanism involving biradical intermediates and not *via* a concerted single step process is now well documented.<sup>5</sup> Therefore, hydrogen bromide quenching of the type II process in 2-P can in principle occur by the trapping of any or all of the following three species: triplet 2-P ( $^3\text{K}$ ); the triplet biradical ( $\text{T}_{\text{R}}$ ); the singlet biradical ( $\text{S}_{\text{R}}$ ).

The Stern-Volmer results provide an estimate of the lifetime of the trapped species if parameters of the trapping rate constant ( $k_{\text{T}}$ ) can be established. For trapping of the 2-pentanone triplet, it is reasonable (see later) to assume a rate constant equal to that observed for the triplet acetone-HBr reaction ( $k_{\text{T}} =$

$10^{9.2-1.1/\theta} \text{ l./mol sec}$ ),<sup>5</sup> and for trapping of either bi-radical species a rate constant like that observed for the ethyl radical-HBr reaction is more appropriate ( $k_{\text{T}} = 10^{9.8-2.3/\theta} \text{ l./mol sec}$ ),<sup>10</sup> These values predict lifetimes for the trapped species of the order  $^X\tau = 8.0 \times 10^3/k_{\text{T}} = 10^{-4.65 \pm 0.05} \text{ sec}$  at the mean reaction temperature (388°K). The rate constant parameters for the reactions of X in the uninhibited reaction are then

$$k_{\text{X}} = (^X\tau)^{-1} = 10^{5.3-1.1/\theta} \text{ sec}^{-1} \quad \text{}^3\text{K trapping} \quad (\text{III})$$

$$k_{\text{X}} = 10^{5.9-2.3/\theta} \text{ sec}^{-1} \quad \text{T}_{\text{R}} \text{ or } \text{S}_{\text{R}} \text{ trapping}$$

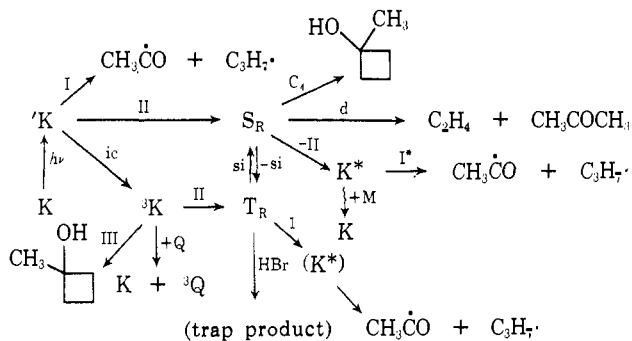
Of the three species ( $\text{S}_{\text{R}}$ ,  $\text{T}_{\text{R}}$ , and  $^3\text{K}$ ), only the triplet biradical can reasonably have Arrhenius parameters for its reaction as low as the above. This conclusion is supported by the following observations.

The rate constant for decomposition of the singlet biradical ( $\text{S}_{\text{R}}$ ) can be estimated by analogy with other singlet 1,4 biradicals, which in turn have been estimated from thermochemical analyses of cyclobutane decompositions.<sup>11</sup> A value of  $k_{\text{d}} = 10^{12.0-6.5/\theta} \text{ sec}^{-1}$  is obtained. This predicts a lifetime of  $10^{-8.4} \text{ sec}$  at 388°K, much too short to be identified with the trapped species.

Similar lifetime considerations exclude trapping of the triplet ketone state. Thus, Wagner<sup>5</sup> reports  $^3\tau(2\text{-pentanone}) = 0.76 \times 10^{-7} \text{ sec}$  (from pentadiene quenching studies in solution). Also, gas phase lifetimes within a factor of 3 of this value have been calculated by us

(10) A. F. Trotman-Dickenson and G. S. Milne, *Nat. Stand. Ref. Data Ser., Nat. Bur. Stand.*, No. 9 (1968).

(11) H. E. O'Neal and S. W. Benson, *J. Phys. Chem.*, 72, 1866 (1968).

Scheme I. Mechanism of the 2-Pentanone Photolysis<sup>a</sup>

	Energetics, <sup>b,c</sup> kcal/mol					
	K	T <sub>R</sub>	S <sub>R</sub>	CH <sub>3</sub> CO	n-C <sub>3</sub> H <sub>7</sub> ·	<sup>3</sup> K <sup>a</sup>
$\Delta H_f^\circ$ (25°)	-61.6	11.0	13.3	-5.4	20.7	18.4
$\Delta H_f^\circ$ (0°K)	-54.4	17.8	20.1	-3.3	25.5	23.6
$(H_{298}^\circ - H_0^\circ)^d$	5.2	5.6	5.6	2.5	3.0	5.2
T <sub>R</sub> → CH <sub>3</sub> CO + n-C <sub>3</sub> H <sub>7</sub> ·				$\Delta H^\circ = \Delta E^\circ = 4.4$ kcal		
S <sub>R</sub> → CH <sub>3</sub> CO + n-C <sub>3</sub> H <sub>7</sub> ·				$\Delta H^\circ = \Delta E^\circ = 2.1$ kcal		
T <sub>R</sub> → <sup>3</sup> (C <sub>2</sub> H <sub>4</sub> ) + CH <sub>3</sub> COCH <sub>3</sub>				$\Delta H_{298}^\circ \approx 22$ kcal <sup>e</sup>		
T <sub>R</sub> → C <sub>2</sub> H <sub>4</sub> + <sup>3</sup> (CH <sub>2</sub> =C(OH)CH <sub>3</sub> )				$\Delta H_{298}^\circ \approx 29$ kcal		

<sup>a</sup> K = ground state 2-pentanone; <sup>1</sup>K = first excited singlet ketone state; <sup>3</sup>K = lowest triplet ketone state; S<sub>R</sub> = singlet 1,4 biradical (2-pentanone 2,5 biradical); T<sub>R</sub> = triplet biradical. The processes involved are: I (type I bond fission); II (intramolecular H abstraction to generate T<sub>R</sub> or S<sub>R</sub>); ic (intersystem crossing between ketone states); si and -si (spin inversion between biradicals); C<sub>4</sub> (C<sub>4</sub> cyclization to give process III product); d (decomposition of S<sub>R</sub> to give type II products); -II (inverse of intramolecular H abstraction, II); I\* (type I reaction from vibrationally excited ketone ground state, K\*). <sup>b</sup> Assuming <sup>3</sup>K lies at an energy of 80 kcal/mol above the ground state, the singlet ketone state (<sup>1</sup>K) should lie approximately 8 kcal/mol higher. <sup>c</sup> K\* vibrational excitation above the critical energy for (C-C) bond rupture when formed from S<sub>R</sub>:  $(E - E_0) = -\Delta H^\circ_{\text{decomp}} + (H^\circ_{\text{T}} - H^\circ_{\text{K}}) + E_d = -2.1 + 5.2 + 6.7 = 9.8$  kcal/mol. <sup>d</sup> Values calculated from an assumed set of normal vibration frequencies using methods of statistical thermodynamics. <sup>e</sup>  $\Delta H_f^\circ(\text{CH}_3\text{COCH}_3) = -51.7$ ;  $\Delta H_f^\circ(\text{C}_2\text{H}_4) = 12.5$ ;  $\Delta H_f^\circ(\text{CH}_2=\text{C}(\text{OH})\text{CH}_3) \approx -44.7$ . The lowest energy of triplet ethylene, corresponding to the perpendicular state, has been calculated to be about 72 kcal above the ground state: H. Basch and V. McKoy, *J. Chem. Phys.*, **53**, 1628 (1970). Assuming that the methyl vinyl alcohol triplet energy is similarly placed relative to its ground state, we estimate  $\Delta H_f^\circ(\text{C}_2\text{H}_4) = 84.5$  kcal/mol and  $\Delta H_f^\circ(\text{CH}_2=\text{C}(\text{OH})\text{CH}_3) \approx 27.3$  kcal/mol.

from available data on biacetyl<sup>1,12</sup> and 1,3-pentadiene<sup>1,13</sup> quenching (see Table III). These estimates, which give  $\tau(^3\text{K}) \approx 2.4 \times 10^{-7}$  sec, are based on the reasonable assumption that quenching rate constants are transferrable between the acetone and 2-pentanone system. The good agreement in calculated lifetimes tends to support this assumption. Thus, with a lifetime of  $10^{-7}$  sec, the chemical trapping of <sup>3</sup>K by HBr seems quite unlikely.

Trapping of <sup>3</sup>K by HBr can also be excluded by considering the Arrhenius parameters expected for the type II reaction from the triplet ketone state. Although, as noted earlier, no reliable values have been obtained for this type of intramolecular H abstraction in the gas phase, Sciano<sup>14</sup> has reported very reasonable values for such type II reactions in the solution photolysis of butyrophenone (B) and valerophenone (V):  $k_{\text{II(B)}} = 10^{11.8-6.65/\theta}$  sec<sup>-1</sup>, and  $k_{\text{II(V)}} = 10^{11.70-4.70/\theta}$

(12) J. Hecklen and W. A. Noyes, Jr., *J. Amer. Chem. Soc.*, **81**, 3858 (1959).

(13) R. E. Rebert and P. Ausloos, *J. Amer. Chem. Soc.*, **87**, 5569 (1965).

(14) P. J. Sciano, *J. Chem. Soc., Chem. Commun.*, 390 (1972).

sec<sup>-1</sup>. The *A* factors are in excellent agreement with those estimated by transition state methods<sup>9</sup> (i.e.,  $A_{\text{II(est)}} = 10^{11.6 \pm 0.3}$  sec<sup>-1</sup>), and the activation energies compare favorably with those for *tert*-butoxy radical H abstraction from hydrocarbons<sup>15</sup> (i.e., 4.8 kcal for tertiary H abstraction; 6.6 kcal for primary H abstraction). Comparable activation energies for triplet intramolecular H abstractions and *tert*-butoxy radical H abstractions are expected in view of the striking correlations in reactivities observed for these two reaction types.<sup>5</sup> Clearly, the deduced Arrhenius parameters of reaction II from our HBr quenching data are incompatible with Sciano's very reasonable parameters, and we conclude, therefore, that hydrogen bromide is not reacting with either the 2-pentanone triplet or the singlet biradical but rather is trapping the triplet 1,4 biradical.

The Stern-Volmer results predict a lifetime for the 2-pentanone 2,5-triplet biradical of between  $10^{-4}$  and  $10^{-5}$  sec and a rate constant for spin inversion of

$$k_{\text{si}} \approx 1.8k_{\text{x}} = 10^{6.2-(2.3 \pm 1.5)/\theta} \text{ sec}^{-1} \quad (IV)$$

Spin inversion, T<sub>R</sub> → S<sub>R</sub>, is the rate-limiting step for the type II reaction of 2-pentanone. These results have important implications relative to controversies regarding so-called "spin correlation effects."<sup>17-19</sup> The Bartlett-Porter explanation of spin correlation holds that singlet biradical reactions occur more rapidly than internal rotations; therefore initial stereochemistries are preserved. In contrast, triplet biradicals must spin invert to the singlet state before reaction can occur. It is proposed that spin inversion is a slow process compared to internal rotation (therefore rate limiting), hence racemization occurs in reactions of T<sub>R</sub> species. It has been shown<sup>17</sup> that the Bartlett-Porter interpretation of spin correlation has two requirements: "high" internal rotation barriers in singlet biradicals ( $V_0 \geq 10$  kcal/mol are required in some systems); and triplet 1,4 biradical spin inversion lifetimes as long as  $10^{-4}$ - $10^{-5}$  sec. Both these requirements have been judged improbable.<sup>17</sup> However, recent INDO calculations<sup>20</sup> show that "some substantial additional barriers to rotation exist in the singlet biradical as a result of through bond interactions which cannot be found in the triplet species," and our present results indicate that triplet 1,4 biradical spin inversion rates can be quite slow, with time periods as long as  $10^{-4}$ - $10^{-5}$  sec. Thus we feel that the Bartlett-Porter explanation of spin correlation effects is essentially correct.

Although this is, perhaps, the first reported trapping

(15) J. A. Kerr and E. Ratajczak, "Second Supplementary Tables of Bimolecular Gas Reactions," University of Wales Institute of Science and Technology, Cardiff, 1969.

(16) The factor of 1.8 difference between  $k_{\text{si}}$  and  $k_{\text{x}}$  follows from a steady state treatment of the mechanism and from available data (see later). The error limits are best estimates based on the estimated error in the activation energy of  $k_{\text{T}}$  and on the estimated error in the temperature dependence of our Stern-Volmer plots (i.e., no apparent *T* dependence).

(17) L. M. Stephenson and J. I. Brauman, *J. Amer. Chem. Soc.*, **93**, 1988 (1971).

(18) P. D. Bartlett and N. A. Porter, *J. Amer. Chem. Soc.*, **90**, 5317 (1968).

(19) L. M. Stephenson, P. R. Covigli, and J. L. Parlett, *J. Amer. Chem. Soc.*, **93**, 1984 (1971).

(20) L. M. Stephenson and T. A. Gibson, *J. Amer. Chem. Soc.*, **94**, 4599 (1972).

**Table III.** Calculation of Triplet 2-Pentanone Lifetimes from Biacetyl and 1,3-Pentadiene Quenching Studies of the Acetone and 2-Pentanone Photochemical Systems

Ref	Quencher-ketone <sup>a</sup>	Method	Results	$k_Q$ , l./((mol sec) <sup>c,e</sup>	$^3\tau$ , sec
2	BA + A $T = 40^\circ$	Stimulated BA emission BA/ $Q_{5000}$ vs. BA	$S/I = k_Q(\text{BA})^3\tau_{(A)}$ $= 230 \text{ Torr}^{-1}$	$2.65 \times 10^{10}$	$1.7 \times 10^{-4.11}$
1	BA + 2-P $T = 32.5^\circ$ $= 56^\circ$	Stimulated BA emission BA/ $Q_{5000}$ vs. BA	$S/I = k_Q(\text{BA})^3\tau_{(2P)}$ $= 0.325 \text{ Torr}^{-1}$ $= 0.306 \text{ Torr}^{-1}$	$(2.65 \times 10^{10})^d$	$2.37 \pm 0.3 \times 10^{-7}$
10	1,3-P + A $T = 32^\circ$	Quenching of decomposition <sup>b</sup> $^3\Phi_d^0/^3\Phi_d$ vs. 1,3-P	$S = k_{Q(1,3-P)}^3\tau_{(A)}$ $= 120 \text{ Torr}^{-1}$	$1.27 \times 10^{10}$	$1.8 \times 10^{-4.11}$
1	1,3-P + 2-P $T = 56^\circ$	Quenching of type II reaction <sup>b</sup> $^3\Phi_d^0/^3\Phi_d$ vs. 1,3-P	$S = k_{Q(1,3-P)}^3\tau_{(2P)}$ $= 0.306 \text{ Torr}^{-1}$	$(1.27 \times 10^{10})^d$	$2.38 \times 10^{-7}$

<sup>a</sup> BA = biacetyl; A = acetone; 1,3-P = 1,3-pentadiene; 2-P = 2-pentanone;  $S$  = slope;  $S/I$  = slope/intercept;  $Q_{5000}$  = observed emission intensity at 5000 Å. <sup>b</sup> Corrected for reactions from the singlet state:  $^3\Phi_d^0/^3\Phi_d = (\Phi_d^0 - \Phi_d)/(\Phi_d - \Phi_d)$ . <sup>c</sup> Quenching rate constants for BA and 1,3-pentadiene are at least an order of magnitude lower than the "usual" assumption of unit collision efficiency for this type of triplet-singlet energy exchange reaction. This apparently erroneous assumption has led to triplet state lifetime estimate factors of 10-100 too short. <sup>d</sup> Quenching rate constants assumed equal in the acetone and 2-pentanone photochemical systems. <sup>e</sup> Absolute quenching rate constants of BA and 1,3-pentadiene toward acetone can be obtained since the lifetimes of the acetone triplet state are well known: W. E. Kaskan and A. B. F. Duncan, *J. Chem. Phys.*, **18**, 427 (1950).

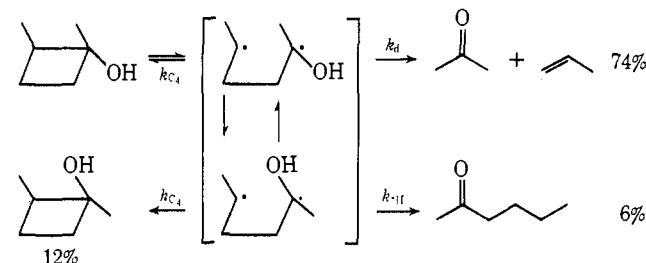
of a 1,4 biradical in the gas phase, Wagner<sup>21</sup> has reported trapping the 1-methoxy-4-phenylbutanol 1,4 biradical, resulting from the photochemically induced type II reaction of  $\gamma$ -methoxybutyrophenone in solution. Various mercaptans were used as trapping agents. Unfortunately, Wagner could not obtain a firm lifetime estimate for the  $T_R$  species because rate data for the trapping reactions were not available. However, his Stern-Volmer results gave  $k_Q\tau \approx 1.8$  (mol/l.)<sup>-1</sup>, and lifetimes comparable to ours would require mercaptan quenching rate constants of  $k_Q \approx 10^6$  l./((mol sec), which are not unreasonable. Note that the trapping mechanism of mercaptans and hydrogen bromide are similar (*i.e.*, both are metathetical radical H abstractions).

The difference observed in the degree of maximum quenching of the type II process effected by different types of quenching agents is significant. Thus,  $^3K$  quenchers (BA and 1,3-P) both quench to  $\Phi_{II}^* \approx 0.10$  (3130 Å), while the  $T_R$  quencher (HBr) gives  $\Phi_{II}^* \approx 0.03$ . According to the mechanism, this means that some photoexcited molecules moving initially through  $S_R$  go to  $T_R$  before reacting. Thus, the reaction modes of  $S_R$  (reactions C<sub>4</sub>, d, and -II) are competitive with spin flip to  $T_R$  at the "low" temperatures of the quenching studies. Type II quantum yields in the presence of excess quencher allow estimates of  $k_{-si}$  and  $K_{si}$  to be made (see later).

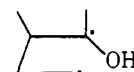
The near constancy of the type II quantum yields with variations in any of the important variables ( $T$ ,  $\lambda$ , and  $P$ ) has a most important mechanistic implication if it is assumed that spin conservation is a requirement of the type II process. Reaction of  $T_R$  to type II products, necessitating the production of either triplet state ethene or triplet state 2-propenol, is endothermic by 20-30 kcal/mol (see energetics of Scheme I); hence, all the type II reaction is relegated to reactions of  $S_R$ . Independence of  $\Phi_{II}$  yields with  $T$ ,  $\lambda$ , and  $P$ , then, requires that all reactions of  $S_R$  have nearly identical activation energies:  $E_d = E_{-II} = E_{C_4}$ . Also, the probability of  $S_R$  formation must remain energy independent. One of the conclusions of the thermochemical kinetic analysis of cyclobutane pyrolysis<sup>11</sup> is that the C<sub>4</sub> cyclization reactions and the decomposition

reactions of  $S_R$  (*i.e.*, singlet 1,4-hydrocarbon biradicals) have comparable rates and comparable activation energies:  $k_{C_4} \approx k_d$ ;  $E_{C_4} \approx E_d \approx 5.9 \pm 1.2$  kcal/mol. The thermal pyrolysis kinetic data (Scheme II) for *cis*-

**Scheme II.** Pyrolysis of *cis*-1,2-Dimethylcyclobutanol<sup>a-c,24</sup>



<sup>a</sup> Other products, ethylene, 2-butanone, and 3-methyl-2-pentanone, are generated from bond rupture to the



biradical. <sup>b</sup> A-factor estimates, following standard transition state estimation methods,<sup>9</sup> give:  $A_d \approx 10^{12.0} \text{ sec}^{-1}$ ;  $A_{C_4} \approx 10^{12.0} \text{ sec}^{-1}$ ;  $A_{-II} \approx 10^{11.0} \text{ sec}^{-1}$ . <sup>c</sup>  $k_{\text{obsd}} = 0.96 \pm 0.11 \times 10^{15-38.0 \pm 1.6/\theta} \text{ sec}^{-1}$  is in good agreement with transition state estimates of the Arrhenius parameters assuming the biradical mechanism above.

1,2-dimethylcyclobutanol (*cis*-1,2-DMCB),<sup>22</sup> a process III product of the 2-hexanone photolysis, are consistent with this near equivalence. Thus (2[yield *trans*-1,2-DMCB]/yield acetone)  $\approx k_{C_4}/k_d \approx 0.33$  at 660°K. The 2-hexanone photochemical quantum yield data at 25° give a somewhat lower value for this rate constant ratio (*i.e.*,  $k_{C_4}/k_d \approx (\Phi_{III}/\Phi_{II})$  singlet = 0.072);<sup>23</sup> however, the difference corresponds to an activation energy variation ( $E_{C_4} - E_d$ ) of only 1.6 kcal/mol. Since the photochemical process III quantum yields are always quite low, the small increase in  $\Phi_{III}$  from  $S_R$  with increasing temperature would not be expected to reflect itself in any significant variation in  $\Phi_{II}$  with  $T$  (as observed in the photochemical studies).

The activation energy equivalence between the inverse type II reaction, -II, and the decomposition reaction, d (required by the type II quantum yield invariance), is perhaps surprising since the former reaction is a six-center, strain free, intramolecular radical-

(21) P. J. Wagner and R. G. Zepp, *J. Amer. Chem. Soc.*, **95**, 287 (1973).

(22) E. D. Feit, *Tetrahedron Lett.*, 1475 (1970).

(23) D. R. Coulson and N. C. Yang, *J. Amer. Chem. Soc.*, **88**, 4511 (1966).

radical disproportionation process generally assumed to have a very low or zero activation energy. However, the *cis*-1,2-DMCB pyrolysis data do suggest that  $E_{-II}$  is roughly equal to  $E_d$ , hence closer to 6 kcal/mol. Thus, the product yield ratio from Scheme II (*i.e.*, yield 2-hexanone/yield acetone  $\approx k_{-II}/k_d \approx 0.08$ ) corresponds closely to the value of the ratio of the estimated  $A$  factors for these reactions ( $A_{-II}/A_d \approx 0.10$ ).

**Type I Process.** At temperatures above 100°, carbonyl radicals formed in type I processes decompose quantitatively.<sup>24</sup> Hence, at  $T > 100^\circ$ , carbon monoxide quantum yields can be equated to  $\Phi_I$  in the pure ketone system. At lower temperatures, acetyl radicals participate in radical-radical recombination and disproportionation reactions; therefore type I yields must be obtained from a stoichiometric relation such as V.

$$\Phi_I = \Phi(\sum_{\text{products}} \text{CH}_3) + \Phi(\sum_{\text{products}} n\text{-Pr}) - \Phi(\text{CO}) \quad (\text{V})$$

where

$$\begin{aligned} \sum_{\text{products}} \text{CH}_3 &= \Phi(\text{CH}_4) + 2\Phi(\text{C}_2\text{H}_6) + \Phi(\text{C}_4\text{H}_{10}) \\ \sum_{\text{products}} n\text{-Pr} &= \Phi(\text{C}_3\text{H}_8) + \Phi(\text{C}_3\text{H}_6) + \\ &\quad \Phi(\text{C}_4\text{H}_{10}) + 2\Phi(\text{C}_6\text{H}_{14}) \end{aligned}$$

Free radicals (both alkyl and carbonyl) are quantitatively trapped by HBr at pressure above 10 Torr even at temperatures as high as 200°. Thus, at "high" HBr pressures,  $\Phi(\text{CO}) \rightarrow 0$ ,  $\Phi(\text{C}_3\text{H}_8) \approx \Phi_I$ , and  $\Phi(\text{CH}_4) \approx \Phi_I$ . Our data (Table II) show that CO and CH<sub>4</sub> yields are almost completely quenched by hydrogen bromide and are roughly equivalent within experimental error in all runs with HBr  $\geq 5$  Torr. Methane and propane quantum yields approach limiting values of 0.015 and 0.10, respectively, in excess HBr. Hence, the maximum contribution of the  $I_b$  split (*i.e.*, to CH<sub>3</sub>· and  $n\text{-C}_3\text{H}_7\dot{\text{C}}\text{O}$ ) is 15% of the total type I process. Since carbon monoxide and methane yields are closely comparable, the actual contribution could be much less.

From Table II, it is apparent that hydrogen bromide is a very efficient quencher of the type I process, particularly at the higher two temperatures. The data suggest that the type I process for pure ketone is temperature dependent between 25 and 125° but is temperature invariant at higher temperatures. As noted before, type I yields at "low" temperatures must be obtained from a stoichiometric relation (eq V). The analytical data of most studies (including this one) are seldom good enough to calculate reliable low-temperature  $\Phi_I$  values. However, the data of Ausloos and Murad (A and M)<sup>25</sup> appear exceptionally good (*i.e.*, good mass balances) and they tend to confirm the low-temperature variation of  $\Phi_I$  with  $T$ . Thus, we calculate from the A and M data:  $\Phi_I = 0.14$  (25°), and  $\Phi_I = 0.21$  (83°). This aspect of the type I process, however, still needs clarification since the temperature dependence of the acetyl radical decomposition in the 25–125° could lead to the illusion of a  $T$ -dependent  $\Phi_I$  in the same range.

The present data, then, suggest two reaction pathways to type I products: a reaction which can be quenched by HBr and which perhaps also increases

(24) J. G. Calvert and J. N. Pitts, "Photochemistry," Wiley, New York, N. Y., 1966.

(25) P. Ausloos and E. Murad, *J. Amer. Chem. Soc.*, **80**, 5929 (1958).

with increasing  $T$ , and a reaction which is both  $T$  and HBr invariant.

One explanation of the HBr-dependent type I reaction involves the generation of vibrationally excited ground state molecules ( $K^*$ ) *via* an inverse type II reaction ( $-II$ ) from the  $S_R$  state. Observations in solution, which show high quantum yields of racemization at the  $\gamma$ -carbon position of optically active ketones capable of type II reactions,<sup>5,26–28</sup> confirm that the inverse type II reaction is a major if not dominant primary process in these photochemical systems. Deactivation of  $K^*$  to the ground state would necessarily occur in solution; however, decomposition to type I products and collisional deactivation could be competition in the gas phase. Although very attractive, this thesis is probably not the correct explanation of the HBr-dependent type I process. An examination of the energetics of Scheme I shows that the vibrational excitation of  $K^*$  (formed from  $S_R$ ) above the critical energy for dissociation to  $\text{CH}_3\dot{\text{C}}\text{O} + n\text{-Pr}$  radicals ( $\Delta E^\circ$ ) is probably no more than 10 kcal/mol. With a molecule as large as 2-P, it is unlikely that spontaneous decomposition at these energies could occur more rapidly than collisional deactivation.<sup>29</sup> In addition, type I product formation *via*  $S_R$  and  $K^*$  would also require (in view of the high quantum yields of  $\gamma$ -carbon racemization and of nonradiative decay) that  $S_R$  react back to the ketone at least as rapidly as it reacts to type II products (*i.e.*, that  $k_{-II}/k_d \geq 1$ ). The *cis*-1,2-DMCB pyrolysis data (Scheme II) indicate that decomposition of  $S_R$  (in that system) is much faster than reaction to the ketone. It is reasonable to assume that the relative reactivities of the  $S_R$  biradicals of the 2-pentanone and 2-hexanone systems are comparable and further that the results for  $S_R$  reactions in the pyrolysis and photochemical systems must correlate. Hence, considering the *cis*-1,2-DMCB pyrolysis data, the condition that  $k_{-II} \geq k_d$  in the photolysis systems seems unlikely.

To explain the HBr-dependent type I reaction in 2-P, and the large quantum yields of  $\gamma$ -carbon racemization and nonradiative decay in other ketone systems, it seems necessary to propose some unusual direct reactions of the triplet biradical state. Thus, in the 2-P photolysis,  $T_R$  species (even at 25°) have sufficient energy to react more or less directly to type I products (see Scheme I). Such a reaction could be described as a spin allowed, inverse type II reaction of the  $T_R$  state producing  $^3K$  molecules in an unstable region well along their normal type I decomposition reaction coordinate (*i.e.*, at a point after the energy maximum). High yields of nonradiative decay, or regeneration of ground state ketone, in other ketones (*e.g.*, 2-hexanone) could entail a conformationally induced spin inversion of  $T_R$ . Thus, if a close proximity of the unpaired electrons of the triplet state (as in the six-center conformation of the  $-II$  reaction transition state) facilitates the  $T_R \rightarrow S_R$  reaction, then the  $S_R$  species so formed would have a higher than normal probability of undergoing the  $-II$  reaction. Operationally, this would act

(26) N. C. Yang and D.-D. H. Yang, *J. Amer. Chem. Soc.*, **80**, 2913 (1958).

(27) K. H. Schulte-Elte and G. Ohloff, *Tetrahedron Lett.*, 1143 (1964).

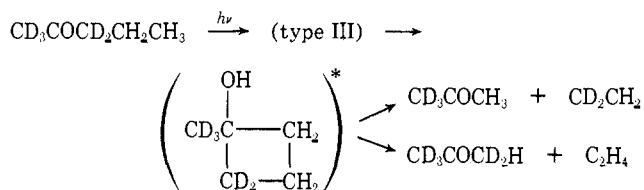
(28) N. C. Yang, A. Morduchowitz, and D. H. Yang, *J. Amer. Chem. Soc.*, **85**, 1017 (1963).

(29) P. J. Robinson and K. A. Holbrook, "Unimolecular Reactions," Wiley, New York, N. Y., 1972.

like a direct  $T_R \rightarrow {}^3K$  process. These reactions are admittedly highly speculative. Yet unless the deductions which appear to require their formulation are gravely in error (which further data on cyclobutanol pyrolysis could clarify), only a still more complex and speculative mechanism can accommodate the present data.

With regard to the  $T$ - and  $HBr$ -independent type I process, it is not possible to decide which of the two excited ketone states ( ${}^1K$  or  ${}^3K$ ) are the immediate precursor state. However, since type I yields are negligible in aromatic ketones which undergo type II reactions,<sup>5</sup> and since these ketones react exclusively *via* the triplet ketone state, the singlet ketone ( ${}^1K$ ) seems the most logical state of origin for this type I process.

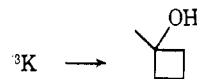
**Processes III.** Dependence of the gas phase process III quantum yields on temperature, pressure, and wavelength and the complete independence of these yields relative to  $T$  and  $\lambda$  changes in solution provide firm evidence for the participation of vibrationally "hot" species in the gas phase III process. The two most reasonable explanations for this behavior have been outlined by Ausloos and Rebbert:<sup>7</sup> (1) spontaneous decomposition of vibrationally hot cyclobutanol products, or (2) preferential reaction to process III products from the lower vibrational levels of some precursor state. The first possibility was adequately eliminated<sup>7</sup> by showing that no  $CD_2CH_2$  is produced in the photolysis of 2-pentanone-1,1,1,3,3- $d_5$  over a wavelength range from 2537 to 3130 Å even at pressures as low as 0.5 Torr. As illustrated below, this is a required product of the spontaneous decomposition of any "hot" cyclobutanol product molecules formed in the photolysis.



The gas phase  $P$ ,  $T$ , and  $\lambda$  effects on  $\Phi_{III}$  then must be a result of the second possibility, and the following reasoning suggests that the triplet ketone ( ${}^3K$ ) is the precursor state responsible. The possibilities are  $S_R$ ,  $T_R$ , and  ${}^3K$ . Since all reaction modes of  $S_R$  have comparable activation energies, the relative reactivities of  $S_R$  cannot be strongly energy dependent (as are the  $\Phi_{III}$  yields). The lifetime of  $T_R$  is quite long compared to collision frequencies; hence, if  $T_R$  were the precursor state, there could be no variation in  $\Phi_{III}$  with total pressure (contrary to experimental observations). The precursor state, then, must be the triplet ketone state. A direct, spin forbidden, low-activation energy and entropy, concerted isomerization of  ${}^3K$  to 1-methylcyclobutanol seems required by the data. Although this interpretation is again not attractive from a theoretical standpoint, it is nevertheless completely consistent with the triplet ketone quenching data:  $\Phi_{III}/\Phi_{II}$  ratios decrease with added 1,3-P in solution and with  $O_2$  and  $NO$  in the gas phase. Stronger quenching of process III relative to the type II process could not occur if both processes occurred only from the same state (e.g., from  $S_R$ ). Thus, a second formation reaction mode for process III products, such as from  ${}^3K$ ,

very sensitive to triplet ketone quenching is required. Similar data and reasoning have led Yang<sup>23</sup> to conclude that process III is predominantly a triplet state reaction. It is interesting to note that the gas phase  $\Phi_{III}/\Phi_{II}$  ratios approach the same limiting value (i.e.,  $\Phi_{III}/\Phi_{II} \sim 0.10$ ) at low pressures, at high temperatures, and at short wavelengths.<sup>7</sup> This ratio, then, is probably a good measure of the relative rates of  $C_4$  cyclization to decomposition for reaction from the singlet biradical state ( $S_R$ ) at photochemical study temperatures:  $k_{C_4}/k_d \simeq 0.10$  ( $T = 25-150^\circ$ ).

**General Comments.** In accommodating the data with the mechanism, it has been necessary to propose three highly speculative and intuitively unattractive reactions:  $T_R \rightarrow CH_3\dot{C}O + n\text{-Pr}\cdot$  (2-P);  $T_R \rightarrow K^*$  (higher ketones)



All three involve electronic state changes which are not easily rationalized by usual kinetic theories. While it is most probable that the data, or mechanism, or deductions which seem to require these processes harbor some error, it is also possible that these "unusual" reactions do occur. Thus, Hammond<sup>30</sup> has suggested that chemical reactions of excited states involving spin changes should be treated in terms of radiationless decay theory rather than *via* normal kinetic theories.

**Rate Constant Evaluations.** If the mechanism is correct, the data provide estimates of some of the rate constants and rate constant ratios. A steady state analysis gives the following relations

$${}^1\Phi_I = k_1/A \quad (\text{VI})$$

$$\Phi_{II} = \frac{k_d k_{II}}{DA} \left[ 1 + \frac{k_{si} k_{io}}{C B} \right] / \left[ 1 - \frac{k_{si} k_{-si}}{C D} \right] \quad (\text{VII})$$

$$\Phi_{III} (\text{from } {}^3K) = k_{III} k_{io} / BA \quad (\text{VIII})$$

$$\frac{\Phi_{II}^0 - \Phi_{II}^*}{\Phi_{II} - \Phi_{II}^*} = 1 + \left[ k_T(HBr) / k_{si} \left( 1 - \frac{k_{-si} k_{si}}{D C'} \right) \right] \quad (\text{IX})$$

where

$$A = k_I + k_{II} + k_{io}$$

$$B = k_{II} + k_{III} + k_Q Q \quad (Q = {}^3K \text{ quencher})$$

$$C = k_1 + k_{si} + k_T(HBr)$$

$$D = k_{C_4} + k_d + k_{-II} + k_{-si}$$

$$C' = k_1 + k_{si}$$

$${}^1\Phi_I = \text{type I yields in excess HBr}$$

The 25° condition is employed in the following analysis since the data are not sufficient to fully examine the very intriguing temperature dependencies of the various reactions.

The Stern-Volmer equation (eq IX) justifies the constant of eq IV,<sup>16</sup> and we will show that at 25° the term  $[1 - (k_{si}/C')(k_{-si}/D)]^{-1} \simeq 1.8$ .

**${}^3K$  Reactions.** The limiting type I quantum yield of 2-P in excess HBr is 0.10. Therefore, from eq VI

$$k_1/A = 0.10 \text{ and } (k_{II} + k_{io})/A = 0.90$$

The reported intersystem crossing quantum yield for 2-P (in solution) is  $\Phi_{io} = k_{io}/A = 0.81$ .<sup>5</sup> Assuming a

(30) G. S. Hammond, *Advan. Photochem.*, **7**, 373 (1969).

similar value for the gas phase reaction gives

$$k_{II}/A = 0.09 \text{ and } k_{ic}/k_{II} = 9.0$$

If we further assume that the rate constant for type II reaction from the  ${}^1K$  state is essentially the same as the rate of reaction from the  ${}^3K$  state (this seems reasonable since spin effects should not much influence an intramolecular H-abstraction process) and that the type II Arrhenius parameters are similar to those obtained by Sciano for butyrophenone in solution,<sup>14</sup> then  $k_{II} \simeq 10^{11.8-6.7/\theta} \simeq 8 \times 10^6 \text{ sec}^{-1}$  ( $25^\circ$ ). Since  $1/A$  is the lifetime of the singlet ketone state, we then obtain  $\tau({}^1K) = 0.09/k_{II} = 1.12 \times 10^{-8} \text{ sec}^{-1}$  ( $25^\circ$ ). This compares very favorably with the singlet ketone gas phase lifetime reported by Wettack and Noyes<sup>1</sup> of  $2.9 \times 10^{-8} \text{ sec}$ .

**${}^3K$  Reactions.** The process III quantum yield originating from the triplet ketone state can be used to obtain values for  $k_{III}/B$ ,  $k_{II}/B$ , and  $k_{ic}/B$ . Thus from eq VIII with

$$\Phi_{III} \text{ (from } {}^3K) = \left[ \left( \frac{\Phi_{III}^0}{\Phi_{II}^0} \right) - \left( \frac{\Phi_{III}}{\Phi_{II}} \right) \right] \Phi_{II}^0 =$$

pure ketone excess Q

$$[0.25 - 0.10](0.30) = 0.045$$

and  $k_{ic}/A = 0.81$  we obtain

$$k_{III}/B = 0.06 \quad k_{II}/B = 0.94$$

$$k_{ic}/B = k_{ic}/k_{II} \quad k_{II}/B = 8.5$$

These values suggest that 6% of the thermolyzed  ${}^3K$  molecules at room temperature react directly to form cyclobutanol products and predict a  ${}^3K$  lifetime of  ${}^3\tau = 1/B = 0.94/k_{II} = 1.1 \times 10^{-7} \text{ sec}$  ( $25^\circ$ ). This estimate is again in excellent agreement with the lifetimes deduced for the  ${}^3K$  species from the 1,3-P and BA quenching studies (see Table III).

**$S_R$  Reactions.** In excess HBr, all  $T_R$  species formed are trapped. These include those produced from reactions of  $S_R$  as well as those formed from the  ${}^3K$  state. From eq VI, the type II quantum yield in excess HBr is

$$\Phi_{C_2H_4}(\text{excess HBr}) = (k_d/D)(k_{II}/A) = 0.025$$

Hence,  $k_d/D = 0.28$ , and

$$\frac{k_d + k_{C_4} + k_{-II} + k_{-si}}{k_d} = 3.58$$

The dominant reaction mode of the  $S_R$  biradical is decomposition. This is clearly evident from the 1,2-DMCB decomposition results. If we assume that the relative rate of decomposition and inverse type II reaction for the  $S_R$  biradical formed in the thermal decomposition of 1,2-DMCB is the same as that for the  $S_R$  biradical of 2-P, then  $k_{-II}/k_d \simeq 12$ , and since  $k_{C_4}/k_d \simeq 0.10$ , we obtain from the above (for  $T = 25^\circ$ )

$$k_{-si}/k_d = 2.38 \text{ and } k_{-si}/D = 0.57$$

This is an interesting result since an absolute value for  $k_{-si}$  can then be obtained from estimates of  $k_d$ . Thus, using the value suggested for the decomposition of the hexyl 2,5 biradical ( $k_d \simeq 10^{12.0-6.5/\theta} \text{ sec}^{-1}$ ) gives<sup>11</sup>  $k_{-si} \simeq 4.6 \times 10^7 \text{ sec}^{-1}$  ( $25^\circ$ ). When coupled with our determination of  $k_{si}$ , one obtains an equilibrium constant for the biradical equilibrium,  $S_R \rightleftharpoons T_R$ , of

$$K_{S \rightarrow T} = (k_{-si}/k_{si}) = 1.1 \times 10^3 \text{ (} 25^\circ \text{)}$$

Assuming a zero activation energy for the singlet to triplet reaction provides estimates of the spin inversion reaction enthalpy and entropy.

$$\Delta H^\circ_{S \rightarrow T} = -E_{si} \simeq -2.3 \text{ kcal}$$

$$\Delta S^\circ_{S \rightarrow T} = 6.2 \text{ eu}$$

These values seem reasonable. The  ${}^3K$  and  ${}^1K$  states of ketones differ in energy by about 5–8 kcal/mol.<sup>24</sup> As the distance between radical centers increases, energy interactions must decrease; hence smaller energy differences are expected for 1,4 biradicals. On the other hand, a well-defined triplet spectrum in the esr of pentamethylene<sup>31</sup> indicates that interaction energies are not zero in this 1,5 biradical. Hence, the 2.3 kcal/mol energy separation between  $S_R$  and  $T_R$  of the 2-pentanol 2,5 biradical obtained above seems possible. The rather large reaction entropy of 6.2 eu can be accounted for in terms of the spin change ( $\Delta S^\circ_{\text{spin}} = R \ln 3 = 2.2 \text{ eu/mol}$ ) and in terms of lower barriers to the three internal rotations between radical centers in the triplet biradical. A 1.3 eu/rotor increase is suggested by the reaction entropy. This is well within the range possible for rotational barrier effects<sup>32</sup> and, as the calculations of Stephenson and Gibson indicate, is an entirely reasonable result.

**$T_R$  Reactions.** We have argued that the photochemical and pyrolysis data for biradical reactions require a reaction of the 2-P triplet biradical directly to type I products. The extent of this reaction can be estimated from the quantum yields required for the temperature- and HBr-dependent type I reaction (eq X).

$\Phi_I^*$  (T and HBr dependent) =

$$\frac{k_1 k_{II}}{C A} \frac{[(k_{ic}/B) + (k_{-si}/D)]}{[1 - ((k_{si}/C)(k_{-si}/D)]} \quad (X)$$

In the absence of HBr,  $\Phi_I^* \simeq 0.30$  and  $C = C'$ . Then, since  $k_1/C' = (1 - (k_{si}/C'))$  and all rate constant ratios are known other than  $k_{si}/C'$ , we calculate from eq X

$$k_{si}/C' = 0.79 \text{ and } k_1/C' = 0.21$$

Thus, the extent of  $T_R$  reaction leading "directly" to type I products need not be large ( $\sim 20\%$ ) to accommodate the pyrolysis and photolysis data.

It is clear from the above that a reasonable, semi-quantitative, description of the 2-pentanone photochemical system is provided by the proposed mechanism. Yet numerous problems remain which can only be resolved by further study. In particular, the temperature dependence of both  ${}^3K$  and  $T_R$  quenching needs to be more thoroughly investigated and also the temperature dependence of the product yields of the related cyclobutanol pyrolysis. Such data would not only provide a good test of mechanism but would also contribute significantly to our understanding of biradical and excited state reactions.

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