The Mercury $6(^3P_0)$ Photosensitized Decomposition of Propane

J. M. Campbell, O. P. Strausz,* and H. E. Gunning

Contribution from the Department of Chemistry,
University of Alberta, Edmonton, Alberta. *Received May 12, 1972*

Abstract: The Hg $6(^3P_0)$ atom sensitized decomposition of propane has been studied. Metastable atoms were produced by the spin–orbit relaxation of $^3P_1$ atoms with nitrogen and the primary *n*-propyl and isopropyl radical yields determined from the measured yields of the isomeric hexane products as a function of nitrogen and propane concentrations at various temperatures after making appropriate allowance for all secondary reactions. The primary quantum yield for propane decomposition is less than unity and increases with temperature: $\Phi(63°) = 0.57 \pm 0.12$ and $\Phi(200°) = 0.95 \pm 0.12$. The primary *n*-propyl to isopropyl radical yield ratio varies according to the rate expression $\log (k_n/k_i) = -0.09 \pm 0.14 - [(1900 \pm 200)/2.3RT]$.

The intervention of Hg $6(^3P_0)$ atoms (Hg^0) in a wide variety of Hg $6(^3P_1)$ (Hg*) photosensitization systems has been established unequivocally in recent years.[1-5] One particularly important class of such systems is represented by the paraffins, the Hg* sensitized decomposition of which has been the focus of interest for several decades.[6] It has now become evident that what had been thought to be the Hg* sensitized decomposition of paraffins is in fact a composite system where Hg* and Hg^0 sensitized decompositions occur concurrently.

For this reason and also because of the inherent interest in Hg^0 sensitizations from the standpoint of our understanding of the mechanism of electronic energy transfer reactions of metal atoms, a study of the Hg^0 + propane system was undertaken. The particular choice of substrate was dictated by our previous studies on the $Hg^* + C_3H_8$ system,[7] and the availability of necessary kinetic data for the complete quantitative treatment of the experimental results.

Experimental Section

The circulatory reaction system and lamp were similar to the one described earlier[8] but with a total volume of 1520 or 755 cm³. Initially the radiation from the lamp was passed through a Vycor filter and, at later stages of the work, a filter containing $NiSO_4$–$CoSO_4$ and "ultraviolet dye"[9] was used to eliminate possible interference from the 4358-, 4047-, 3125-, and 3130-Å lines emitted by the lamp. The transmission of the filter solution through a 2-cm path was less than 1% at each of the above wavelengths. No significant difference in the product yields was noted with the additional filter.

In a typical experiment, propane was measured into the circulating system, then nitrogen was added to a total pressure of about 1140 Torr (or in some experiments 940 Torr). The mixture was then circulated for 30 min with the saturator at −78° and then 30 min at 0°. Irradiation time varied from 5 to 25 min depending on lamp intensity, but conversion of propane was kept lower than 0.15% except in the four runs at very low $[C_3H_8]/[N_2]$ ratios where the conversions were nearly 1%. Experiments which included measurements of the product quantum yields were done with the saturator at room temperature to ensure complete absorption. After irradiation, nitrogen was circulated through two traps at −198° to remove the condensable materials and then carefully pumped off. Excess propane was distilled off at −139° and the fraction not volatile at this temperature, consisting of propylene and isomeric hexanes, was analyzed by gas chromatography on a 40% isoquinoline column.

Two grades of nitrogen were used. In most experiments (Linde) commercial grade gas was purified by passing it through a column of copper turnings at 270° and then through a molecular sieve at −78°. Control experiments at each temperature and all quantum yield measurements were done with high purity nitrogen (Airco) containing maximum impurities of 2 ppm. The purification of propane and the method of calculation of primary *n*-propyl and isopropyl radical yields from the isomeric hexane products have been described.[8]

Quantum yields were based on intensities measured by propane[10] or nitrous oxide[11] actinometry.

Results

As in previous studies,[12,13] Hg^0 atoms were produced by the spin–orbit relaxation of Hg* atoms with nitrogen. Because of its high spin–orbit relaxation efficiency and chemical inertness, nitrogen has been widely used for generating Hg^0 atoms for kinetic studies. Recently it has been shown[3,4] that propane itself also produces Hg^0 atoms in small concentrations. This, however, does not cause insurmountable difficulties in the evaluation of the kinetic data for the individual reaction of Hg* and Hg^0 atoms with propane.

The yields of the three isomeric hexane products, *n*-hexane (Hx), 2-methylpentane (MP), and 2,3-dimethylbutane (DMB) were determined as a function of propane and nitrogen pressures at various temperatures. The results are presented in Table I along with computed values of some kinetic functions described below. Initial radical yields were evaluated in terms of the following reactions

$$\mathrm{Hg} + h\nu\ (2537\ \text{Å}) \rightleftharpoons \mathrm{Hg}^* \tag{1}$$

$$\mathrm{Hg}^* + \mathrm{C_3H_8} \longrightarrow (\mathrm{HgC_3H_8})^* \tag{2}$$

$$(\mathrm{HgC_3H_8})^* \longrightarrow i\text{-Pr} + \mathrm{H} + \mathrm{Hg} \tag{3}$$

$$\longrightarrow n\text{-Pr} + \mathrm{H} + \mathrm{Hg} \tag{4}$$

$$\longrightarrow \mathrm{C_3H_8} + \mathrm{Hg}^0 \tag{5}$$

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Table I. Product Yields and Rate Functions in the Mercury Photosensitization of Various Propane–Nitrogen Mixtures at Different Temperatures

Time, min	C_3H_8, Torr	N_2, Torr	[DMB], μmol	[MP], μmol	[Hx], 10^3 μmol	$\frac{2R_{(n)}}{R_{(n+i)}}$	F	β	χ[a]	Y[b]
$T = 27°$										
7.0	15.1	963	0.151	0.0153	0.39	0.081	0.100	0.081		0.037
20.1	29.9	910	0.782	0.0922	2.71	0.093	0.198	0.134		0.049
12.2	30.0	910	0.083	0.0089	0.24	0.086	0.199	0.134		0.042
6.0	30.2	920	0.217	0.0259	0.77	0.095	0.198	0.133		0.051
6.0	49.9	901	0.268	0.0308	0.89	0.091	0.316	0.178		0.043
5.0	74.1	868	0.177	0.0218	0.67	0.098	0.456	0.215		0.054
$T = 63°$										
27.0	4.9	1052	0.076	0.012	0.49	0.125	0.034	0.033	0.20	0.062
14.0	9.5	1140	0.221	0.029	0.95	0.103	0.052	0.049		0.041
25.0	9.9	1038	0.177	0.026	0.94	0.115	0.058	0.055	0.46	0.052
23.0	9.9	906	0.178	0.024	0.81	0.106	0.065	0.061	0.45	0.044
24.0	12.1	995	0.127	0.017	0.56	0.105	0.071	0.066	0.30	0.042
6.0	12.4	990	0.181	0.025	0.84	0.107	0.073	0.067		0.045
25.0	12.6	906	0.198	0.027	0.89	0.105	0.080	0.073	0.42	0.043
25.0	16.4	910	0.234	0.033	1.13	0.109	0.100	0.070	0.53	0.047
15.0	17.2	1123	0.263	0.033	1.01	0.098	0.087	0.079		0.037
20.0	17.2	1004	0.144	0.020	0.70	0.110	0.096	0.086	0.36	0.047
25.0	19.4	990	0.248	0.033	1.07	0.104	0.107	0.096	0.65	0.041
20.0	20.3	906	0.203	0.030	1.14	0.118	0.121	0.106	0.59	0.055
21.0	26.3	908	0.200	0.027	0.90	0.105	0.151	0.129	0.55	0.043
6.0	28.2	927	0.257	0.038	1.43	0.117	0.158	0.133		0.054
12.0	28.9	910	0.244	0.037	1.40	0.117	0.164	0.138		0.056
14.0	32.6	1127	0.295	0.036	1.08	0.096	0.152	0.129		0.034
25.0	33.2	1004	0.148	0.024	0.95	0.125	0.170	0.142	0.48	0.063
20.0	40.0	906	0.230	0.033	1.17	0.112	0.219	0.175	0.65	0.050
25.0	41.1	1007	0.157	0.021	0.73	0.107	0.205	0.166	0.47	0.045
5.0	50.5	905	0.154	0.023	0.88	0.119	0.267	0.205		0.056
12.0	58.5	1097	0.258	0.034	1.12	0.104	0.259	0.199		0.042
6.5	61.0	912	0.230	0.034	1.24	0.115	0.315	0.231	0.70	0.053
5.0	68.8	867	0.205	0.030	1.09	0.114	0.363	0.256		0.052
10.0	81.3	1074	0.241	0.033	1.14	0.108	0.350	0.249		0.046
19.0	88.1	906	0.257	0.036	1.26	0.110	0.430	0.288	0.97	0.048
20.0	88.6	906	0.260	0.039	1.45	0.117	0.432	0.289	0.90	0.055
13.0	156.2	920	0.183	0.029	1.13	0.123	0.724	0.395	1.12	0.061
13.0	234.4	740	0.193	0.030	1.20	0.123	1.015	0.469	1.35	0.061
25.0	321.0	680	0.240	0.039	1.61	0.128	1.287	0.498	1.78	0.069
60.0	470.0	480	0.694	0.125	5.60	0.139	1.735	0.580	2.05	0.078
73.0	640.0	240	0.686	0.133	6.44	0.149	2.211	0.625	2.32	0.089
$T = 124°$										
14.0	9.7	1141	0.197	0.039	1.97	0.153	0.062	0.059		0.060
14.0	11.6	1120	0.217	0.046	2.43	0.161	0.070	0.067		0.067
12.0	17.8	1137	0.306	0.044	2.35	0.163	0.090	0.085		0.069
11.0	27.8	908	0.135	0.030	1.63	0.167	0.146	0.132		0.073
100.0	29.8	1135	1.546	0.343	18.98	0.168	0.130	0.119		0.075
12.0	30.8	1124	0.230	0.048	2.49	0.159	0.134	0.122		0.066
11.0	53.1	1100	0.242	0.048	2.37	0.152	0.209	0.181		0.058
11.0	60.8	1108	0.246	0.053	2.89	0.165	0.232	0.198		0.072
11.0	78.1	1077	0.218	0.048	2.65	0.167	0.290	0.239		0.075
$T = 166°$										
14.0	8.2	1160	0.184	0.053	3.80	0.214	0.079	0.075		0.097
12.0	17.2	1175	0.148	0.041	2.97	0.211	0.104	0.097		0.095
12.7	29.0	1135	0.243	0.070	5.10	0.215	0.141	0.128		0.100
11.5	30.4	910	0.198	0.058	4.24	0.217	0.166	0.149		0.102
11.0	38.1	1133	0.196	0.056	4.05	0.214	0.166	0.150		0.099
11.0	59.6	1105	0.202	0.060	4.35	0.217	0.230	0.199		0.104
12.8	82.3	1082	0.244	0.074	5.63	0.224	0.295	0.246		0.113
$T = 200°$										
25.0	66.3	820	0.189	0.062	5.06	0.239	0.316	0.262	1.06	0.115
25.0	151.0	784	0.198	0.062	4.79	0.229	0.575	0.419	1.25	0.117
23.0	239.0	680	0.198	0.063	4.95	0.232	0.858	0.551	1.54	0.132
22.0	349.0	605	0.191	0.057	4.27	0.221	1.15	0.657	1.71	0.135
22.0	428.0	514	0.182	0.056	4.29	0.226	1.38	0.727	1.77	0.155
60.0	550.0	350	0.511	0.147	10.55	0.213	1.77	0.822	1.92	0.153
72.0	700.0	125	0.614	0.170	11.74	0.206	2.31	0.923	2.28	0.163

[a] $\chi = \Phi_T\{1 + (\sigma^{2*}/\sigma^{2\circ})_{C_3H_8}(k_{11}/k_2)([Hg][N_2]/[C_3H_8]) + F[1 - \Phi' + (k_{-1}/k_2[C_3H_8])]\}$. [b] $Y = 2R_{(n)}/R_{(n+i)} - k_{13}/(k_{12}/k_{13}) + \delta Q_3$.

$$(\mathrm{HgC_3H_8})^* \longrightarrow \mathrm{C_3H_8} + \mathrm{Hg} + h\nu' \tag{6}$$

$$\mathrm{Hg^0} + \mathrm{C_3H_8} \longrightarrow (\mathrm{HgC_3H_8})^0 \tag{7}$$

$$(\mathrm{HgC_3H_8})^0 \longrightarrow i\text{-Pr} + \mathrm{H} + \mathrm{Hg} \tag{8}$$

$$\longrightarrow n\text{-Pr} + \mathrm{H} + \mathrm{Hg} \tag{9}$$

$$\longrightarrow \mathrm{C_3H_8} + \mathrm{Hg} + h\nu'' \text{ and/or other processes} \tag{10}$$

$$\mathrm{Hg^0} + \mathrm{Hg} + \mathrm{M} \longrightarrow \mathrm{Hg_2}^* + \mathrm{M} \tag{11}$$

$$\mathrm{H} + \mathrm{C_3H_8} \longrightarrow i\text{-Pr} + \mathrm{H_2} \tag{12}$$

$$\longrightarrow n\text{-Pr} + \mathrm{H_2} \tag{13}$$

$$n\text{-Pr} + \mathrm{C_3H_8} \rightleftarrows i\text{-Pr} + \mathrm{C_3H_8} \tag{14}$$

$$2n\text{-Pr} \longrightarrow n\text{-hexane (Hx)} \tag{15}$$

$$\longrightarrow \mathrm{C_3H_6} + \mathrm{C_3H_8} \tag{16}$$

$$i\text{-Pr} + n\text{-Pr} \longrightarrow \text{2-methylpentane (MP)} \tag{17}$$

$$\longrightarrow \mathrm{C_3H_6} + \mathrm{C_3H_8} \tag{18}$$

$$2i\text{-Pr} \longrightarrow \text{2,3-dimethylbutane (DMB)} \tag{19}$$

$$\longrightarrow \mathrm{C_3H_6} + \mathrm{C_3H_8} \tag{20}$$

$$\mathrm{Hg}^* + \mathrm{N_2} \rightleftarrows \mathrm{Hg^0} + \mathrm{N_2} \tag{21}$$

where the third body M is N_2 and C_3H_8. Further reactions of Hg_2^* are not included since they cannot lead to production of propyl radicals. Quenching of Hg* atoms by nitrogen in its $\nu = 0$ level, reaction 21 probably produces vibrationally excited ($\nu = 1$) nitrogen, but at the low-light intensities and high pressures used in the present system N_2 ($\nu = 1$) is rapidly relaxed to the zero level and does not play a major role in the kinetics.[12]

(a) Other Reactions. As shown by Back,[10] the effect of self-scavenging by the reaction

$$\mathrm{H} + \mathrm{C_3H_6} \longrightarrow n\text{-Pr or } i\text{-Pr} \tag{22}$$

is important in the Hg* photosensitization of propane even at a few tenths of a per cent conversion. Since $(k_{12} + k_{13})/k_{22} = 1.4 \exp(-4800/RT)$,[14] it can be estimated that even under the most favorable conditions (27°, 10 Torr of propane, and 1000 Torr of nitrogen), a maximum of about 11% of the hydrogen atoms are consumed in reaction 22. At higher temperatures and propane pressures, the contribution of reaction 22 is less than 5% and can be neglected in the following calculations. Note that reaction 22 has no effect on quantum yield determinations because it also leads to the production of a propyl radical.

The occurrence of the reaction

$$2\mathrm{H} + \mathrm{M} \longrightarrow \mathrm{H_2} + \mathrm{M} \tag{23}$$

where M is either the wall of the reaction vessel or an inert gas molecule, could interfere with the basic kinetic scheme. However, at the pressures used in these experiments the wall reaction could not compete effectively with recombination or abstraction.[12] The rate of gas-phase recombination can be estimated from the steady-state equation for [H]: $R_{23}/R_{12+13} = k_{23}[\mathrm{M}] \cdot R_{(n+i)}/2[\mathrm{C_3H_8}]^2(k_{12} + k_{13})^2$. Larkin[15] found k_{23} (M = Ar) to be 4.6×10^{15} cm^6 mol^{-2} sec^{-1} at 291°K with a temperature dependence of $T^{-1/2}$ or larger.[16,17] Assuming $k_{12} + k_{13} = 10^{12.7} \exp(-7400/RT)$ cm^3 mol^{-1} sec^{-1} [18] and conditions most favorable to reaction 23, $R_{23}/R_{12+13} = 1.6 \times 10^{-2}$, that is, about 2% of the hydrogen atoms react by recombination rather than abstraction from propane. Since k_{23} decreases and $k_{12} + k_{13}$ increases with increasing temperature, R_{23}/R_{12+13} must decline rapidly with increasing temperature or propane pressure. Consequently an error of a factor of 2 in the value used for k_{23} (M = N_2), would be compensated for by the square terms and it is therefore reasonable to neglect reaction 23 in the kinetic scheme.

(b) Decomposition Quantum Yields. The overall quantum yield of decomposition of propane in a mixture of mercury, nitrogen, and propane irradiated with 2537-Å radiation is given by

$$\Phi_\mathrm{T} = \frac{R_{3+4} + R_{8+9}}{R_{-1} + R_2 + R_7 + R_{11} - R_5}$$

where R_{3+4} is the combined rate of reactions 3 and 4, R_{-1} is the rate of spontaneous emission of the Hg* atom, etc. This can be written in terms of measurable quantities and known rate constants from the steady-state treatment of reactions 1 through 21 (see Appendix for derivation) as in eq 24

$$\Phi_\mathrm{T}\left[1 + \left(\frac{\sigma^{2*}}{\sigma^{2\circ}}\right)_{\mathrm{C_3H_8}} \frac{k_{11}[\mathrm{Hg}][\mathrm{N_2}]}{k_2[\mathrm{C_3H_8}]} + F\left(1 - \Phi' + \frac{k_{-1}}{k_2[\mathrm{C_3H_8}]}\right)\right] = \Phi^*F + \Phi^0 \tag{24}$$

where

$$F = \left[\frac{\sigma^{2*}}{\sigma^{2\circ}}\right]_{\mathrm{C_3H_8}}\left\{\frac{[\mathrm{Hg}^*]}{[\mathrm{Hg}^0]}\right\} = \frac{\left\{\left(\frac{\sigma^{2*}}{\sigma^{2\circ}}\right)_{\mathrm{C_3H_8}} K_{21}^{-1} + \frac{k_2}{k_{21}}\frac{[\mathrm{C_3H_8}]}{[\mathrm{N_2}]} + \left(\frac{\sigma^{2*}}{\sigma^{2\circ}}\right)_{\mathrm{C_3H_8}} \frac{k_{11}[\mathrm{Hg}][\mathrm{A}]}{k_{21}[\mathrm{N_2}]}\right\}}{\left\{1 + \Phi'\frac{[\mathrm{C_3H_8}]}{[\mathrm{N_2}]}\frac{k_2}{k_{21}}\right\}}$$

and

$$\Phi' = k_5/(k_3 + k_4 + k_5 + k_6)$$

$$\Phi^* = (k_3 + k_4)/(k_3 + k_4 + k_5 + k_6)$$

$$\Phi^0 = (k_8 + k_9)/(k_8 + k_9 + k_{10})$$

Thus Φ^* and Φ^0 can be evaluated if the terms on the left-hand side of eq 24 are known. There are several values available in the literature for the rate constants and kinetic parameters required in the calculation. The ones which have been employed in the present study are listed in Table II. Plots of the left-hand side of eq 24 (represented by χ) against F at 63 and 200° are summarized in Table III and shown in Figure 1. The curvature observed in this plot at 63° below $F = 0.2$ is probably due to loss of radicals by the reactions

$$\mathrm{H} + n\text{-Pr} \longrightarrow \mathrm{C_3H_8} \tag{25}$$

$$\mathrm{H} + i\text{-Pr} \longrightarrow \mathrm{C_3H_8} \tag{26}$$

An estimate of the rates of reactions 25 and 26, compared to abstraction of H atoms from propane by hydrogen, can be made from the rate of the analogous reaction with ethyl radicals.

$$\mathrm{H} + \mathrm{C_2H_5} \longrightarrow \mathrm{C_2H_6} \tag{27}$$

Assuming $k_{25} + k_{26} \approx k_{27} = 2.3 \times 10^{13}$ cm^3 mol^{-1}

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Table II. Values of the Input Parameters Used in the Calculation of k_9/k_8 and k_4/k_3

Quantity	Value	Ref
$\sigma^{2*}{}_{C_3H_8}$	3.1 Å^2	*a*
$(\sigma^{2*}/\sigma^{2°})_{C_3H_8}$	5.6	12
k_2/k_{21}	$6.5 \exp[(1/T - 1/300)1600/R]$	*a, b*
k_{11}	3.8×10^{18} cc^2 mol^{-2} sec^{-1}	12
K_{21}	$3 \exp(-5000/RT)$	*c*
k_{-1}	Calculated from $\tau_0 = 1.08 \times 10^{-7}$ sec corrected for imprisonment	*d*
Φ'	0.38 and 0.14	3, 23
k_{16}/k_{15}	0.154	*e*
k_{18}/k_{17}	0.408	*e*
k_{20}/k_{19}	0.69	*e*

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Table III. Values of Decomposition Quantum Yields Calculated from the Data Shown in Figure 1 for $F > 0.2$[a]

Temp, °C	Φ^*	Φ^0
63	0.84 ± 0.10	0.57 ± 0.12
200	0.58 ± 0.08	0.95 ± 0.12
	Self-Consistent Values	
63	0.95 ± 0.10	0.59 ± 0.12
200	0.54 ± 0.10	0.94 ± 0.12

[a] Error limits correspond to standard deviations.

sec^{-1} [19] and $k_{15} = 10^{13.8}$ cm^3 mol^{-1} sec^{-1},[20] the ratio

$$\frac{R_{25+26}}{R_{12+13}} = \frac{(k_{25} + k_{26})[n\text{-Pr}]/[i\text{-Pr}]R_{HX}{}^{1/2}}{(k_{12} + k_{13})[C_3H_8]k_{15}{}^{1/2}}$$

is approximately 0.3 (at 25° and 10 Torr of propane) and decreases at higher pressures and temperatures. However, reactions 25 and 26 would have little effect on the calculated *n*-propyl/isopropyl ratio since both rate constants are near the collision frequency and $k_{25}/k_{26} \approx 1$.

It is seen from Table III that Φ^* decreases and Φ^0 increases with rising temperature but the total quantum yield of decomposition in Hg* sensitization, $\Phi^* + (1 - \Phi^*)\Phi^0$, is close to unity and varies little with temperature.[7]

(c) Calculation of the Ratio k_9/k_8. A steady-state treatment of reactions 1–21 leads to the following expression for the fractional yield of *n*-propyl radicals (*cf.* Appendix)

$$\frac{2R_{(n)}}{R_{(n+i)}} = Q_4 + \frac{k_{13}}{k_{12} + k_{13}} - \delta Q_3 \qquad (28)$$

where

$$Q_4 = \frac{k_9}{k_8 + k_9} + \left[\frac{k_4}{k_3 + k_4} - \frac{k_9}{k_8 + k_9}\right]\beta$$

$$\beta = F\Phi^*/(\Phi^0 + F\Phi^*)$$

$$\delta = \frac{2\{1 - \exp(-\epsilon[\text{Hg}]L/2)\}}{\{\epsilon[\text{Hg}](1 - \exp(-\epsilon[\text{Hg}]L))\}}$$

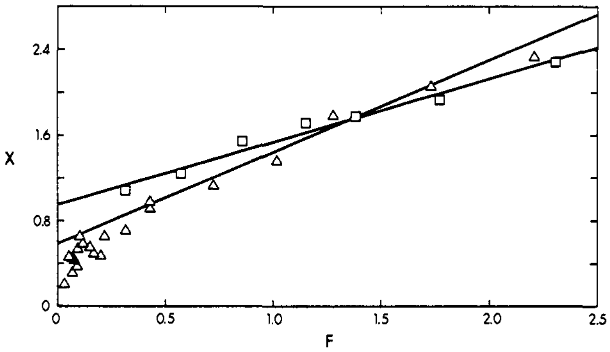

Figure 1. Variation of the quantum yield eq 24 with F: (△) 63°, (□) 200°.

and

$$Q_3 = \frac{R_{DMB}{}^{1/2}}{R_{(n+i)}}\left(\frac{R_{MP}}{R_{DMB}} - 2K_{14}{}^{-1}\right)\frac{k_{14}}{k_{19}{}^{1/2}}[C_3H_8]$$

This mechanism predicts a linear dependence of the quantity $2R_{(n)}/R_{(n+i)} - k_{13}/(k_{12} + k_{13}) + \delta Q_3$ on the expression β, with the intercept given by $k_9/(k_8 + k_9)$. Computed quantities from experiments at five temperatures are summarized in Table IV and displayed in Figures 2 and 3. An Arrhenius plot of k_9/k_8 calculated from these values is shown in Figure 4. A least-mean-squares calculation of these points gives

Table IV. Summary of Results from Figures 2 and 3

Temp, °C	Points	Slope[a]	Intercept[b]
27	6	0.11 ± 0.04	0.031 ± 0.006
63	31	0.057 ± 0.008	0.041 ± 0.002
124	9	0.03 ± 0.04	0.064 ± 0.005
166	7	0.10 ± 0.01	0.087 ± 0.002
200	7	0.08 ± 0.01	0.089 ± 0.006

[a] $k_4/(k_3 + k_4) - k_9/(k_8 + k_9)$. [b] $k_9/(k_8 + k_9)$.

$$\log k_9/k_8 = -0.09 \pm 0.14 - \frac{1900 \pm 200}{2.3RT}$$

where the error limits represent standard deviations. Thus

$$k_9/k_8 = 0.83 \exp(-1900/RT)$$

Discussion

The foregoing computations of Φ^*, Φ^0, and k_9/k_8 are based on the available rate constants listed in Table II. The effect of errors in the input data on the calculated kinetic parameters can be examined by varying the input values over a small range. Since the disproportionation to combination ratio k_{20}/k_{19} for isopropyl radicals has been shown to be independent of temperature (within 0.5 kcal/mol) between 26 and 207°,[21] it is reasonable to assume that k_{16}/k_{15} and k_{18}/k_{17} do not change with temperature either. If, however, k_{16}/k_{15} increases with temperature, $\Delta E°$, ΔE^*, and $\Delta E° - \Delta E^*$ increase slightly but remain within the limits of estimated error, ±20%.

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(19) M. J. Kurylo, N. C. Peterson, and W. Braun, *J. Chem. Phys.*, **53**, 2776 (1970).

(20) E. L. Metcalfe and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 4620 (1962).

(21) P. Cadman, T. Inel, and A. F. Trotman-Dickenson, *J. Chem. Soc. A*, 1207 (1970).

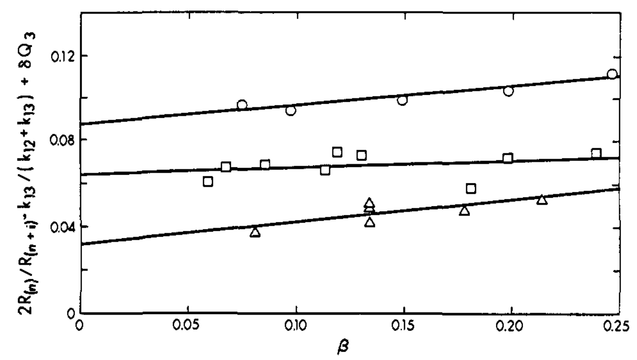

Figure 2. Plots of the quantity $2R_{(n)}/R_{(n+i)} - k_{13}/(k_{12} + k_{13}) + \delta Q_3$ from eq 28 against β: (△) 27°, (□) 124°, (○) 166°.

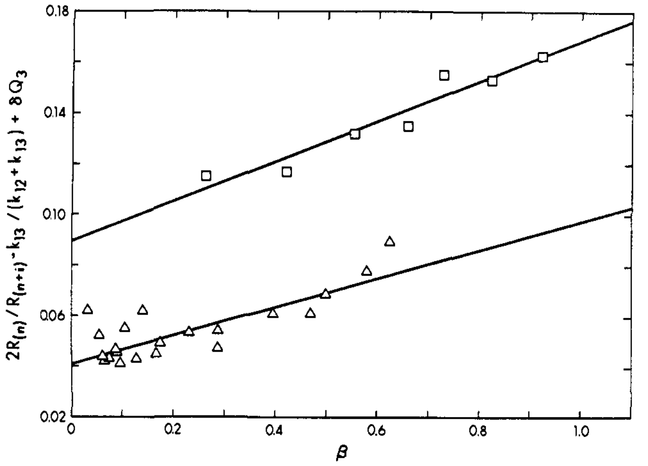

Figure 3. Plots of the quantity $2R_{(n)}/R_{(n+i)} - k_{13}/(k_{12} + k_{13}) + \delta Q_3$ from eq 28 against β: (△) 63°, (□) 200°.

Values for $(\sigma^{2*}/\sigma^{2\circ})_{C_3H_8}$ ranging from 5.6 to 290 have been reported.[3,12,13,22] Employing a value of 25 rather than 5.6, as quoted in Table II, yields $k_9/k_8 = 0.62 \exp(-1800/RT)$. The use of quenching cross-section ratios larger than 30, however, is incompatible with the present results since this leads to negative values for $k_9/(k_8 + k_9)$ at 27° (the intercept of Figure 2).

At the time of our earlier study[7] on the $Hg^* + C_3H_8$ reaction the role of Hg^0 atoms in the system was uncertain. In the meantime it has become evident[3,23] that Hg^0 atoms form in the system although the quantum yield of formation, Φ', is still somewhat uncertain. It is now possible to reassess our earlier value, $\log k_4/k_3 = -0.206 - 1072/2.3RT$), for the relative rate expression of *n*-propyl to isopropyl radical formation by making appropriate allowance for the intervention of Hg^0 atoms. Taking the higher reported value of Φ', 0.38, the rate expression becomes

$$\log k_4/k_3 = -0.05 \pm 0.08 - \frac{1260 \pm 180}{2.3RT}$$

Thus, $\Delta E^\circ - \Delta E^* = 0.68$ kcal/mol. Lowering the value of Φ' has the effect of increasing $\Delta E^\circ - \Delta E^*$, which becomes 1.0 kcal/mol at $\Phi' = 0.2$.

Two additional relative rate expressions can be derived from the present data. Assuming that the

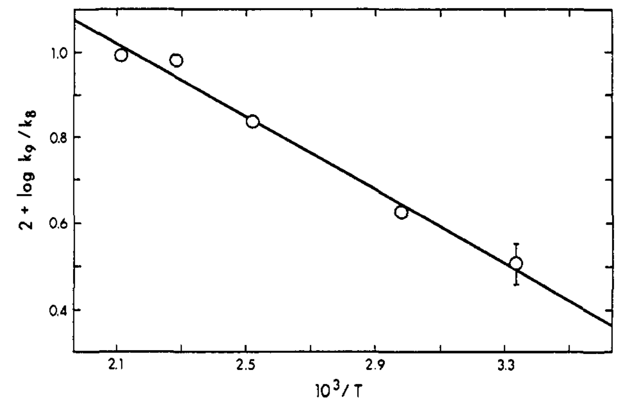

Figure 4. Arrhenius plot of the *n*-propyl/isopropyl yield ratio (k_9/k_8) from the Hg^0 sensitized decomposition of propane.

quantum yield of band fluorescence in the Hg^* system is negligible compared with other processes, the relative rate expression

$$k_5/k_3 \approx 32 \exp(-3000/RT)$$

is obtained from the values of Φ^* and the k_4/k_3 ratio computed above. Also from the temperature variation of Φ^0 one obtains

$$k_8/k_{10} \approx 2 \times 10^4 \exp(-6600/RT)$$

A knowledge of these ratios allows us to compute Φ^* and Φ' at any temperature. Furthermore, since Φ' is required for the calculation of F in eq 24, an iterative computation can be carried out by placing the resulting values of Φ' into F and redetermining the quantities of Φ^* and Φ^0. Self-consistency is achieved for the following values of the Arrhenius parameters: $k_5/k_3 = 1.2 \times 10^3 \exp(-6600/RT)$, $k_4/k_3 = 0.55 \exp(-1000/RT)$, and $k_9/k_8 = 0.88 \exp(-2000/RT)$. It should be noted that the self-consistent value of Φ', 0.05 (63°), is in better agreement with the recent determination of Vikis, *et al.*,[23] than of Callear and McGurk.[3]

Thus far the rate processes were treated as being in thermal equilibrium. In reality they represent typical nonequilibrium systems energized by thermal preactivation through the reagents, propane and mercury, and by chemical activation through the enthalpy change of complex formation. The enthalpy change for the $Hg^* + C_3H_8$ system is -3.9 kcal/mol and for the $Hg^0 + C_3H_8$ system is probably somewhat less, about -3.0 kcal/mol. Therefore a more appropriate form of the relative rate expressions would be, $k/k' = A/A' \exp(-\Delta E/R(T_0 + T))$, where T_0 is the temperature of the chemical activation. The value of T_0 can be estimated with some approximations from the enthalpy changes and the known specific heats of propane and mercury. The correction term then changes with temperature and its contribution amounts to 15-60% of the thermal energization. Plotting now the experimental rate constant ratios against $(T_0 + T)^{-1}$, the following rate expressions are obtained: $k_4/k_3 = 2.6 \exp(-2600/R \cdot (T_0 + T))$, $k_9/k_8 = 2.8 \exp(-3300/R(T_0 + T))$, and for the self-consistent set $k_4/k_3 = 1.2 \exp(-2200/R(T_0 + T))$ and $k_9/k_8 = 2.4 \exp(-3300/R(T_0 + T))$.

We consider the latter parameters as the best values, and assign the activation energies 2.2 and 3.3 kcal/mol to the energy separations of the respective potential energy surface intersections. The difference of 1.1 kcal/mol in the activation energies, $\Delta E^\circ - \Delta E^*$, sug-

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(22) A. C. Vikis and H. C. Moser, *J. Chem. Phys.*, **53**, 1491 (1970); 233 (1970).

(23) A. C. Vikis, G. Torrie, and D. J. Le Roy, *Can. J. Chem.*, **50**, 176 (1972).

gests that the hydrogen abstraction reactions for the $^3P_1$ and $^3P_0$ systems proceed on distinctly different reaction surfaces. These surfaces intersect at energies above the *n*-propyl forming steps but the Arrhenius parameters cannot be reliably assessed from the present study. The values determined for ΔE^* and ΔE°, 2.2 and 3.3 kcal/mol, are in general agreement with those reported for the H-atom transfer reactions of paraffins with H atoms and alkyl radicals.[24]

At room temperature, the Hg ($^3P_1$) atom sensitized decomposition of propane proceeds with quantum efficiencies: $\Phi^*(i\text{-Pr}) = 0.88$; $\Phi^*(n\text{-Pr}) = 0.09$; and $\Phi^*(\mathrm{Hg}^0) = 0.03$. The quantum yield of band emission can be estimated to be less than about 0.01. The quantum efficiencies of the processes in the Hg ($^3P_0$) atom sensitization of propane are as follow: $\Phi^0(i\text{-Pr}) = 0.21$; $\Phi^0(n\text{-Pr}) = 0.01$; Φ^0(emission and/or other processes) ~ 0.78. The collision induced spin–orbit relaxation $^3P_1 \rightarrow {}^3P_0$ in the $^3P_1$ system is temperature dependent and increases with increasing temperature. Also the ratio *n*-Pr/*i*-Pr in both systems increases with temperature. The low quantum yield of decomposition in the $^3P_0$ system is puzzling and, as shown in the accompanying article, cannot be accounted for in terms of efficient competition with band emission. The only plausible process for energy dissipation appears to be intersystem crossing to the ground state.

From comparison of the quantum yield values with the known quenching rate constants, the upper limits of the energy barriers for dissociation of the complexes $\mathrm{Hg^*\cdot C_3H_8}$ and $\mathrm{Hg^0\cdot C_3H_8}$ *via* the repulsive surface, *i*-Pr + HHg, are estimated to be 2.1 and 3.7 kcal/mol above the reactant state, or 6.1 and 6.7 kcal/mol above the bottom of the potential well, respectively.

The results obtained here on the $\mathrm{Hg^0 + C_3H_8}$ system and in our previous study on the $\mathrm{Hg^* + C_3H_8}$ system should be of general validity and apply with appropriate modification to all paraffin systems. A further discussion of mechanistic details is presented in the light of semiempirical bond-energy–bond-order calculations in one of the accompanying articles.

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Appendix

(a) Derivation of the Expressions for F and Φ_T. The steady-state equations for $[(\mathrm{HgC_3H_8})^*]$, $[\mathrm{Hg^0}]$, and $[(\mathrm{HgC_3H_8})^0]$ are

$$\mathrm{d}[(\mathrm{HgC_3H_8})^*]/\mathrm{d}t = k_2[\mathrm{Hg^*}][\mathrm{C_3H_8}] - (k_3 + k_4 + k_5 + k_6)[(\mathrm{HgC_3H_8})^*] = 0 \quad (29)$$

$$\mathrm{d}[\mathrm{Hg^0}]/\mathrm{d}t = k_5[(\mathrm{HgC_3H_8})^*] + k_{21}[\mathrm{Hg^*}][\mathrm{N_2}] - k_{-21}[\mathrm{Hg}]^0[\mathrm{N_2}] - k_{11}[\mathrm{Hg^0}][\mathrm{Hg}][\mathrm{M}] - k_7[\mathrm{Hg^0}][\mathrm{C_3H_8}] = 0 \quad (30)$$

$$\mathrm{d}[(\mathrm{HgC_3H_8})^0]/\mathrm{d}t = k_7[\mathrm{Hg^0}][\mathrm{C_3H_8}] - (k_8 + k_9 + k_{10})[(\mathrm{HgC_3H_8})^0] = 0 \quad (31)$$

Substitution of the expression for $[(\mathrm{HgC_3H_8})^*]$ from eq 29 into (30) and solving for $[\mathrm{Hg^*}]/[\mathrm{Hg^0}]$ yields

$$\frac{[\mathrm{Hg^*}]}{[\mathrm{Hg^0}]} = \frac{k_{-21}[\mathrm{N_2}] + k_{11}[\mathrm{Hg}][\mathrm{M}] + k_7[\mathrm{C_3H_8}]}{k_2\Phi'[\mathrm{C_3H_8}] + k_{21}[\mathrm{N_2}]}$$

Division of the numerator and denominator by $k_{21}[\mathrm{N_2}]$ and multiplication of this expression by $(\sigma^{2*}/\sigma^{2\circ})_{\mathrm{C_3H_8}}$ ($= k_2/k_7$) gives

$$F = (\sigma^{2*}/\sigma^{2\circ})_{\mathrm{C_3H_8}}[\mathrm{Hg^*}]/[\mathrm{Hg^0}] = \frac{(\sigma^{2*}/\sigma^{2\circ})_{\mathrm{C_3H_8}}K_{21}{}^{-1} + \dfrac{k_2[\mathrm{C_3H_8}]}{k_{21}[\mathrm{N_2}]} + \left(\dfrac{\sigma^{2*}}{\sigma^{2\circ}}\right)_{\mathrm{C_3H_8}}\dfrac{k_{11}[\mathrm{Hg}][\mathrm{M}]}{k_{21}[\mathrm{N_2}]}}{1 + \Phi'\dfrac{k_2[\mathrm{C_3H_8}]}{k_{21}[\mathrm{N_2}]}} \quad (32)$$

where

$$K_{21}{}^{-1} = k_{-21}/k_{21}$$

$$\Phi' = k_5/(k_3 + k_4 + k_5 + k_6)$$

The overall quantum yield of propyl radicals is given by their rate of production divided by the sum of all possible modes of deactivation of excited mercury

$$\Phi_T = \frac{R_{3+4} + R_{8+9}}{R_{-1} + (1 - \Phi')R_2 + R_7 + R_{11}}$$

where $R_{3+4} = (k_3 + k_4)\,[(\mathrm{HgC_3H_8})^*]$, etc. Division by R_2 and expansion gives

$$\Phi_T = \frac{\Phi^* + \Phi^0 k_7[\mathrm{Hg^0}]/k_2[\mathrm{Hg^*}]}{\dfrac{k_{-1}}{k_2[\mathrm{C_3H_8}]} + (1 - \Phi') + \dfrac{k_7[\mathrm{Hg^0}]}{k_2[\mathrm{Hg^*}]} + \dfrac{k_{11}[\mathrm{Hg^0}][\mathrm{Hg}][\mathrm{M}]}{k_2[\mathrm{Hg^*}][\mathrm{C_3H_8}]}}$$

Thus from the expression for F, eq 32, we have

$$\Phi_T\left\{1 + \left(\frac{\sigma^{2*}}{\sigma^{2\circ}}\right)_{\mathrm{C_3H_8}}\frac{k_{11}[\mathrm{Hg}][\mathrm{M}]}{k_2[\mathrm{C_3H_8}]} + F\left(1 - \Phi' + \frac{k_{-1}}{k_2[\mathrm{C_3H_8}]}\right)\right\} = \Phi^* F + \Phi^0 \quad (24)$$

(b) Derivation of k_4/k_3 and k_9/k_8 Ratios for Propane and Propane–Nitrogen Mixtures. The steady-state equations for [*n*-Pr], [*i*-Pr], and [H] in this system are given by

$$\mathrm{d}[n\text{-Pr}]/\mathrm{d}t = k_4[(\mathrm{HgC_3H_8})^*] + k_9[(\mathrm{HgC_3H_8})^0] + k_{13}[\mathrm{H}][\mathrm{C_3H_8}] - \{k_{14}[n\text{-Pr}] - k_{-14}[i\text{-Pr}]\}[\mathrm{C_3H_8}] - (k_{15} + k_{16})[n\text{-Pr}]^2 - (k_{17} + k_{18})[n\text{-Pr}][i\text{-Pr}] = 0$$

$$\mathrm{d}[i\text{-Pr}]/\mathrm{d}t = k_3[(\mathrm{HgC_3H_8})^*] + k_8[(\mathrm{HgC_3H_8})^0] + k_{12}[\mathrm{H}][\mathrm{C_3H_8}] + \{k_{14}[n\text{-Pr}] - k_{-14}[i\text{-Pr}]\}[\mathrm{C_3H_8}] - (k_{17} + k_{18})[n\text{-Pr}][i\text{-Pr}] - (k_{19} + k_{20})[i\text{-Pr}]^2 = 0$$

$$\mathrm{d}[\mathrm{H}]/\mathrm{d}t = (k_3 + k_4)[(\mathrm{HgC_3H_8})^*] + (k_8 + k_9)[(\mathrm{HgC_3H_8})^0] - (k_{12} + k_{13})[\mathrm{H}][\mathrm{C_3H_8}] = 0$$

These are related to the experimental quantities $R_{(n)}$ and $R_{(n+i)}$ by

$$R_{(n)} = (k_{15} + k_{16})[n\text{-Pr}]^2 + (k_{17} + k_{18})[n\text{-Pr}][i\text{-Pr}]$$

$$R_{(n)} = k_4[(\mathrm{HgC_3H_8})^*] + k_9[(\mathrm{HgC_3H_8})^0] + k_{13}[\mathrm{H}][\mathrm{C_3H_8}] - \{k_{14}[n\text{-Pr}] - k_{-14}[i\text{-Pr}]\}[\mathrm{C_3H_8}]$$

$$R_{(n+i)} = (k_{15} + k_{16})[n\text{-Pr}]^2 + (k_{17} + k_{18})[n\text{-Pr}][i\text{-Pr}] + (k_{19} + k_{20})[i\text{-Pr}]^2 = (k_3 + k_4)[(\mathrm{HgC_3H_8})^*] + (k_8 + k_9)[(\mathrm{HgC_3H_8})^0] + (k_{12} + k_{13})[\mathrm{H}][\mathrm{C_3H_8}]$$

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(24) A. F. Trotman-Dickenson, *Advan. Free-Radical Chem.*, **1**, 1 (1965).

and from $d[H]/dt$

$$R_{(n+i)} = 2(k_3 + k_4)[(HgC_3H_8)^*] + 2(k_8 + k_9)[(HgC_3H_8)^0]$$

or

$$R_{(n+i)} = 2(k_{12} + k_{13})[H][C_3H_8]$$

Division of $R_{(n)}$ by $R_{(n+i)}$ including the contribution from the nonuniform absorption of light[25] gives

$$2R_{(n)}/R_{(n+i)} = Q_4 + k_{13}/(k_{12} + k_{13}) - \delta Q_3 \quad (28)$$

where

$$\delta = \frac{2\{1 - \exp(-\epsilon[Hg]L/2)\}}{\{\epsilon[Hg](1 - \exp(-\epsilon[Hg]L))\}}$$

L is the path length (4 cm) and ϵ is the extinction coefficient of mercury.

$$Q_3 = \{k_{14}[n\text{-Pr}] - k_{-14}[i\text{-Pr}]\}[C_3H_8]/R_{(n+i)} = \frac{R_{DMB}{}^{1/2}}{R_{(n+i)}}\left(\frac{R_{MP}}{R_{DMB}} - 2K_{14}{}^{-1}\right)\frac{k_{14}}{k_{19}{}^{1/2}}[C_3H_8]$$

and

$$Q_4 = \frac{k_4[(HgC_3H_8)^*] + k_9[(HgC_3H_8)^0]}{(k_3 + k_4)[(HgC_3H_8)^*] + (k_8 + k_9)[(HgC_3H_8)^0]}$$

From eq 29 and 31, Q_4 is given by

$$Q_4 = \frac{\dfrac{k_4k_2[Hg^*]}{(k_3 + k_4 + k_5 + k_6)} + \dfrac{k_9k_7[Hg^0]}{(k_8 + k_9 + k_{10})}}{\dfrac{(k_3 + k_4)k_2[Hg^*]}{(k_3 + k_4 + k_5 + k_6)} + \dfrac{(k_8 + k_9)k_7[Hg^0]}{(k_8 + k_9 + k_{10})}}$$

Dividing the numerator and denominator by $k_7[Hg^0]$ and substitution of F, Φ^*, and Φ^0 yield

$$Q_4 = (F\Phi^* + \Phi^0)^{-1}\left\{\frac{k_4F}{(k_3 + k_4 + k_5 + k_6)} + \frac{k_9}{(k_8 + k_9 + k_{10})}\right\} = \frac{k_4}{k_3 + k_4}\beta + \frac{k_9}{k_8 + k_9}(1 - \beta)$$

where

$$\beta = \Phi^*F/(F\Phi^* + \Phi^0)$$

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(25) Reference 6, p 640.

The Mechanism of Energy Transfer in the Triplet Mercury Photosensitization of Paraffins

H. E. Gunning, J. M. Campbell, H. S. Sandhu, and O. P. Strausz*

Contribution from the Department of Chemistry,
University of Alberta, Edmonton, Alberta, Canada. *Received May 12, 1972*

Abstract: A unified mechanistic model accommodating all known experimental observations is proposed for the quenching of the $^3P_1$ and $^3P_0$ states of mercury atoms by the paraffins. The process is viewed as a simple hydrogen abstraction reaction of the divalent, paramagnetic mercury atom in analogy with the well-characterized abstraction reactions of other triplet (but ground state) reagents such as O (^3P), carbenes, nitrenes, etc. The principal differences between ground- and excited-state systems can be summarized in the following points. (i) The excited state transition complex is more stable owing to the higher polarizability of the excited atom as compared to that of ground-state species, has a longer lifetime, and is capable of undergoing radiative transitions, making it amenable to experimental observations through spectroscopic studies. (ii) The presence of a larger number of reaction channels in the excited state renders the excited state chemistry more complex and causes a pronounced departure from simple second-order kinetics on the microscopic scale. The semiempirical bond-energy–bond-order method for the estimation of the energy of activation of ground-state systems can also be applied with appropriate minor modifications to the Hg ($^3P_1$) paraffin systems. The computed energies of activation correctly predict the trend in the experimental rate data.

Early studies on the triplet mercury photosensitized reactions of paraffins date back nearly to the time of discovery of the phenomenon of electronic energy transfer.[1,2] In the intervening years an immense amount of work has been expended on the experimental study of the field. The problems actively explored were centered on the nature of the primary steps involved, together with their quantum efficiencies and absolute rate parameters, the role of the lower lying metastable $^3P_0$ (Hg^0) state of mercury in the reaction sequences, and in a more general context, on the elucidation of the details of the reaction hypersurfaces. To these were later added the spectroscopic problems related to the phenomena of pressure broadening and band fluorescence from the transient complexes formed between the mercury atom and paraffin molecule.

The theoretical framework for the rationalization of the mechanistic details evolved slowly. This can be attributed to several factors. The reactions of electronically excited atoms, as photochemical systems in general, proceed on excited surfaces involving radiative and nonradiative internal transitions. The transition probabilities and the potential surfaces themselves, apart from a few exceptions, are poorly characterized. Therefore conventional rate theories are not readily applicable and because of the high atomic number of

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(1) A. G. G. Mitchell and M. W. Zemansky, "Resonance Radiation and Excited Atoms," Macmillan, New York, N. Y., 1934.

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