Photolysis of Bromotrichloromethane

BY H. W. SIDEBOTTOM, J. M. TEDDER AND J. C. WALTON

Chemistry, Dept. The University, Dundee, Scotland

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Bromotrichloromethane vapour has been irradiated with light of 3650 Å wavelength. The photolysis to trichloromethyl radicals and bromine atoms, as evident from the formation of hexachloroethane, is both pressure and temperature dependent. The effect of the addition of inert gases on the quantum yield was also investigated. The results provide evidence for the existence of electronically excited bromotrichloromethane molecules and suggest that two exicted states may be involved. The data also provide information about the rate of abstraction of chlorine from bromotrichloromethane by trichloromethyl radicals :

 $\operatorname{CCl}_{3} + \operatorname{CCl}_{3}\operatorname{Br} \to \operatorname{CCl}_{4} + \operatorname{CCl}_{2}\operatorname{Br} \cdot k_{b} = (7 \cdot 1 \pm 1 \cdot 0) \times 10^{6} \exp(-10,500 \pm 800)/RT \, \mathrm{l. \ mole^{-1} \ sec^{-1}}.$

Bromotrichloromethane has been used extensively as a source of trichloromethyl radicals.¹ Trichloromethyl radicals, initially formed, can combine to give hexachloroethane, or can react with other species in the system. The rate of hexachloroethane formation is temperature dependent when olefins,² or alkanes ³ are present. Little quantitative information about the photolysis of polyhalogenomethanes is available.⁴ Simons and Yarwood have investigated the flash photolysis of bromotrichloromethane,⁵ and Hautecloque ⁶ has published some work on the photochemical decomposition of bromotrichloromethane at temperatures above 200°. In this paper we report the results of bromotrichloromethane photolysis under a wide variety of initial conditions.

EXPERIMENTAL

MATERIALS

Commercial CCl₃Br was distilled on a Büchi spinning band column, the distillate contained ~0.5 % CCl₄. This was removed by preparative gas chromatography on an Aerograph A700 gas chromatograph. The resulting material was at least 99.9 % pure as shown by analytical gas chromatography. Commercial CF₄ and CO₂ were trap-to-trap distilled and degassed in the usual manner. Commercial samples of C₂Cl₆, CCl₄, CCl₂Br₂ and CCl₂==CCl₂ were used, without purification, for identification purposes.

METHODS

All materials were handled on a conventional vacuum line made of Pyrex. The cylindrical, Pyrex, reaction cell was 8 cm long and had a volume of 167 ml. The light source was an Osram ME/D high pressure compact source mercury arc. A Corning glass filter was used to isolate the 3650 Å region. The incident light intensity was varied by placing gauzes of different mesh sizes in front of the mercury arc. The gauzes were calibrated on an Unicam SP800, u.-v. spectrometer at 3650 Å. The products of the reactions were analyzed on a Griffin and George D6 gas density balance chromatograph. In quantitative analyses the average of about four chromatograms was taken. The identity of the products of a photolysis was determined by comparing the retention times with authentic materials run under exactly the same conditions.

RESULTS

The ultra-violet absorption of bromotrichloromethane vapour was determined using an Ebert spectrograph. The absorption was continuous showing no fine structure, and had a maximum at 2510 Å. A value of the molar extinction coefficient was determined at 3650 Å, ($\varepsilon = 2 \times 10^{-2}$ l. mole⁻¹ cm⁻¹). A variation in temperature of 30° produced no detectable change in the extinction coefficient.

The products of the photolysis in the temperature range 92-200° were Br_2 , CCl_4 , CCl_2Br_2 and C_2Cl_6 . In the experiments at 185 and 200° there were traces of tetrachloroethylene. In another experiment bromotrichloromethane was heated in the reaction vessel at 195° for 18 h in the dark. No traces of product were detected. At 205°, on similar treatment, traces of C_2Cl_6 and bromine were found. Subsequent analytical runs were of duration 3 to 4 h and temperatures were always less than 200°C so that there was no contribution from thermal decomposition. In a photolysis experiment carried out at 280°, where thermal decomposition occurs simultaneously, large amounts of $CCl_2=CCl_2$ were produced in addition to the products observed below 200°.

A series of experiments was carried out in which the incident light intensity was varied. The results are shown in table 1.

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temp. °C	time sec	[CCl ₃ Br]mole l. ⁻¹	[C2Cl6]/[CCl3Br]	transmission %
125	3600	1.17×10^{-3}	1.085×10^{-2}	100
125	3600	1.17×10^{-3}	0.836×10^{-2}	73
125	3600	1.17×10^{-3}	0.442×10^{-2}	39
125	3600	1.17×10^{-3}	0.250×10^{-2}	23

The quantity log $[C_2Cl_6]/[CCl_3Br]$ was plotted against log (% transmission) and gave a straight line. The data for all the individual runs were combined in a least squares calculation and gave a value of 1.01 ± 0.05 for the slope.

A series of photolyses was carried out in which the reaction temperature was varied. The products CCl_4 , CCl_2Br_2 and C_2Cl_6 were quantitatively analyzed and the results are shown in table 2.

 $[CCl_3Br] = 1.17 \times 10^{-3}$ mole $1.^{-1}$; reaction time 4 h

temp. °C	[CCl ₂ Br ₂]/[CCl ₃ Br]	[CCl ₄]/[CCl ₃ Br]	[C2Cl6]/[CCl3Br]	[CCl ₄]/[CCl ₂ Br ₂]
122	2·29×10-4	2.63×10^{-4}	166×10^{-4}	1.15
145	3.23×10^{-4}	3.65×10^{-4}	154×10^{-4}	1.13
159	7·79×10 ⁻⁴	8·54×10 ^{−4}	444×10 ⁻⁴	1.10
170	11·87×10 ⁻⁴	14.78×10^{-4}	535×10-4	1.25
180	14.07×10^{-4}	17.21×10^{-4}	423×10^{-4}	1.22
200	34.1×10^{-4}	43.5×10^{-4}	729×10 ⁻⁴	1.27

Data were plotted in the form $2 + \log [CCl_4]/[CCl_3Br][C_2Cl_6]^{\frac{1}{2}}$ against $10^3/T^{\circ}$. Leastsquares treatment gave a value for the slope $(E_b + \frac{1}{2}E_d)/2\cdot 3R$ of $2\cdot 31 \pm 0.05$, and for the intercept $\log (A_b/A_{\frac{1}{2}})$ of $1\cdot 4 \pm 0\cdot 1$. Similarly, the slope of a plot of $2 + \log [CCl_2Br_2]/$ $[CCl_3Br][C_2Cl_6]^{\frac{1}{2}}$ against $10^3/T^{\circ}$ was $(E_b + \frac{1}{2}E_d)/2\cdot 3R = 2\cdot 27 \pm 0.05$ and the intercept $\log (A_b/A_{\frac{1}{2}})$ was $1\cdot 4 \pm 0\cdot 1$.

All values of quantum yields were based on the value $\phi Fe^{II} = 1.21$ at 22° for potassium ferrioxalate at 3650 Å. The quantum yield of hexachloroethane formation

was determined at various pressures of CCl_3Br between 5 and 40 mm. Photolyses lasted 2 h and the results are shown in table 3.

In another series of experiments, various pressures of inert gases were added to a fixed pressure of CCl_3Br . The quantum yields are shown in table 4. In experiments labelled F, CF_4 was the added inert gas, and in those labelled G it was CO_2 .

	Table	3.—PRESSUE	RE VARIATION	OF QUANT	TUM YIELD	
expt. no.	temp. °C	$\begin{bmatrix} CCl_3Br \end{bmatrix} \\ mole \ l.^{-1} \times 10^3 \end{bmatrix}$	$\frac{[C_2Cl_6]}{[CCl_3Br]} \times 10^3$	¢	$\frac{\phi}{1-\phi}$	$\frac{1-\phi}{[CCl_3Br]}$
D_1	92	1.65	4.47	0.0222	0.0227	592
D_2	90	1.37	5.75	0.0286	0.0294	710
D_3	90	0.88	6.04	0.0302	0.0310	1100
D_4	92	0.55	8.57	0.0428	0 ∙0446	1740
Ci	112	1.65	8.15	0.0406	0.0423	582
$\overline{C_2}$	110	1.10	8.99	0.0448	0·0469	8 68
C ₃	112	0.88	9.20	0.0458	0.0480	1080
C₄	112	0.55	10.88	0.0542	0.0573	1720
\mathbf{E}_{1}	147	1.65	39.1	0.195	0.242	488
$\mathbf{E_2}$	148	1.37	39.4	0.197	0.245	586
E_3	147	0.88	41.2	0.206	0.258	904
E4	149	0.55	42.9	0.214	0.272	1430
E ₅	147	0.28	47.4	0.236	0.310	2730
B ₁	187	2.20	42.3	0.210	0.267	358
\mathbf{B}_2	184	1.65	67.5	0.336	0.207	402
$\bar{B_3}$	185	1.37	66.0	0.330	0.493	490
B₄	184	0.88	65•4	0.326	0.484	766
B ₅	185	0.55	73·4	0.366	0-577	1150
\mathbf{B}_{6}	185	0.28	97·9	0-488	0.953	1830

TABLE 4.—VARIATION OF ϕ with inert gas pressure

 $[CCl_3Br] = 1.38 \times 10^{-3} \text{ mole } 1.^{-1}; \text{ temp. } 148^{\circ}.$

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expt. no.8	[N] (N=CF ₄)×10 ³	$\frac{[C_2Cl_6]}{[CCl_3Br]} \times 10^2$	ø	$\frac{\phi}{1-\phi}$	$\frac{1-\phi}{[\text{CCl}_3\text{Br}]+[\text{N}]}$
F_1	5.52	2.74	0.137	0.158	125
$\mathbf{F_2}$	4.14	2.78	0.138	0.161	156
$\overline{F_3}$	2.76	2.75	0.137	0.159	208
$\mathbf{F_4}$	1.38	3.03	0.151	0.178	308
\mathbf{F}_{5}	0.00	3.94	0.196	0.244	582
	(N=CO ₂)				
G1	8.28	1.63	0.0813	0.0885	95
G ₂	5.52	1.90	0.0948	0.1051	131
G₃	4.14	1.95	0.0970	0.1081	163
G ₄	2.76	2.33	0.1161	0.131	214

DISCUSSION

The overall chemical steps in the photolytic decomposition of bromotrichloromethane below 200°C can be represented as follows:

$$CCl_3Br + hv \rightarrow CCl_3 + Br \qquad (a)$$

$$CCl_3 + CCl_3Br \rightarrow CCl_4 + CCl_2Br$$
 (b)

$$\operatorname{CCl}_2\operatorname{Br} + \operatorname{CCl}_3\operatorname{Br} \to \operatorname{CCl}_2\operatorname{Br}_2 + \operatorname{CCl}_3$$
 (c)

$$\operatorname{CCl}_{3} \cdot + \operatorname{CCl}_{3} \cdot \to \operatorname{C}_{2} \operatorname{Cl}_{6} \tag{d}$$

$$Br \cdot + Br \cdot + M \to Br_2 + M \tag{e}$$

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Chain-carrying steps yield CCl_4 and CCl_2Br_2 as products, whereas chain-terminating steps yield C_2Cl_6 and Br_2 . In all the experiments the ratio of the rate of chain carrying reaction to chain terminating reaction was less than 1; so that the overall processes is in a non-chain region and radical-radical products predominate.

The extinction coefficient of CCl₃Br at 3650 Å is only 2×10^{-2} l. mole⁻¹ cm⁻¹, so to a good approximation $\phi I_a = \phi I_0 \beta l$ [CCl₃Br], where *l* is cell length and $(\beta = 2 \cdot 3\epsilon)$. If termination occurs predominantly by reaction (*d*), the rate of hexachloroethane formation should be proportional to the first power of the incident light intensity. The first series of results given in table 1 confirm this. The gradient of a plot of log [C₂Cl₆]/[CCl₃Br] against log (% transmission) gives the exponent of the light intensity, which was $1 \cdot 01 \pm 0 \cdot 05$.

The mechanism also predicts that the rates of formation of CCl_4 and CCl_2Br_2 should be the same, i.e., that the ratio of the amount of CCl_4 to CCl_2Br_2 in the products should be 1. Column 6 of table 2 shows that this ratio is close to 1 at all temperatures but that there is also a consistent small excess of CCl_4 .

EFFECT OF TEMPERATURE

Application of the steady-state approximation to the mechanism leads to the following relationships:

$$[CCl_4]/[C_2Cl_6] = [CCl_2Br_2]/[C_2Cl_6] = k_b[CCl_3Br](\phi I_a/2k_d)^{\frac{1}{2}},$$

$$d[C_2Cl_6]/dt = \phi I_a/2.$$
(I)
(I)

Arrhenius parameters may therefore be found for the abstraction of chlorine from bromotrichloromethane by CCl₃ radicals, step (b). The combination rate constant k_d is ⁷ $E_d = 0$, $A_d = 10^{10.9}$ l. mole ⁻¹sec⁻¹; this together with the data in table 2, leads to the result,

$$k_b = (7.1 \pm 1.0) \times 10^6 \exp -(10,500 \pm 800)/RT$$
 l. mole⁻¹ sec⁻¹

Hautecloque ⁶ reported a value for $E_b - \frac{1}{2}E_d$ of 18.6 ± 1 kcal/mole. We believe this value to be too high. Hautecloque's experiments were carried out above 200°C where thermal decomposition of CCl₃Br, and consequent increase in the rate of C₂Cl₆ formation occurs. The curvature exhibited by her Arrhenius plot in the region of 200°C could be attributed to the onset of thermal decomposition.

Few quantitative determinations of the rate of halogen abstraction have been reported. Hautecloque found a value of 7.0 kcal/mole for the activation energy of the abstraction of chlorine from hexachloroacetone by CCl_3 radicals.⁸ Alcock and Whittle ⁹ find activation energies for the abstraction of chlorine by CF_3 radicals from CCl_4 of 10.4 kcal/mole from $CHCl_3$ of 12.0 kcal/mole from CH_2Cl_2 of 11.8 kcal/mole and from CH_3Cl of 17 kcal/mole.

The quantum yield of hexachloroethane formation $\phi(C_2Cl_6)$ was determined for a series of CCl₃Br pressures and temperatures (table 3). Since every CCl₃· radical formed in the initial photolytic decomposition eventually becomes part of a hexachloroethane molecule, the quantum yield of CCl₃Br decomposition ϕ is twice $\phi(C_2Cl_6)$. The systematic variation of ϕ with temperture and pressure suggests that the primary photochemical process involves formation of electronically excited CCl₃Br molecules.

Steacie *et al.* have shown that if one electronically excited state is formed, which cannot decompose from its lowest vibrational level then a plot of $\phi/(1-\phi)$ against 1/[reactant] should be linear and pass through the origin.¹⁰ If, however, decomposition can occur from the lowest vibrational level, or if more than one electronically

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excited state is formed, then a positive intercept should be obtained. Plots of $\phi/(1-\phi)$ against $1/[CCl_3Br]$ from the bromotrichloromethane photolysis all gave straight lines with a positive intercept. Hence decomposition occurs directly from the lowest vibrational level of the initial excited state, or a second excited state is formed from the first.

DEACTIVATION IN THE PHOTOLYSIS

Two mechanisms have been advanced to account for vibrational deactivation of the electronically excited state.^{11, 12} In the multistage, or weak, deactivation mechanism a molecule which has reached the *n*th vibrational level S^n by light absorption is deactivated to a low lying level S^o by a series of collisions which progressively degrade the vibrational energy. In the single stage, or strong, mechanism a molecule is degraded from the *n*th vibrational level S^n to the low lying level S^o in a single collision. By analogy with the work on hexafluoroacetone the following mechanism may be proposed to represent the primary process:

$$\operatorname{CCl}_{3}\operatorname{Br} + hv \to S^{n} \tag{1}$$

$$S^n \to CCl_3 + Br$$
 (2, *n*)

$$S^n + \mathbf{M} \to S^{n-1} + \mathbf{M} \tag{3, n}$$

$$S^1 \rightarrow CCl_3 + Br$$
 (2, 1)

$$S^1 + M \to S^\circ + M \tag{3, 1}$$

$$S^{\circ} \rightarrow CCl_{3}Br + hv_{f} \tag{4}$$

$$S^{\circ} \rightarrow CCl_{3}Br$$
 (5)

$$S^{\circ} \rightarrow T^{\circ}$$
 (6)

$$T^{\circ} \rightarrow \text{CCl}_{3}\text{Br} + hv_{p} \tag{7}$$

$$T^{\circ} \rightarrow \text{CCl}_{3^{\circ}} + \text{Br}_{\bullet}$$
 (8)

$$T^{\circ} \rightarrow \text{CCl}_{3}\text{Br}$$
 (9)

S and T represent two electronically excited states, probably a singlet and a triplet, and the superscripts indicate vibrational energy. For strong deactivation the series of steps (2, n), (3, n) are replaced by two only, (2) and (3). Application of the steady-state approximation to this mechanism leads to eqn. (III) or (IV):

$$\frac{\phi}{1-\phi} = \frac{1}{1-\phi_{\infty}} \prod_{i=1}^{n} (1+k_{2,i}/k_{3,i}[\text{CCl}_3\text{Br}])^{-1}, \quad (\text{III})$$

or, for strong deactivation,

$$\phi/(1-\phi) = [1/(1-\phi_{\infty})](1+k_2/k_3[\text{CCl}_3\text{Br}]) - 1, \tag{IV}$$

where $\phi_{\infty} = k_6 k_8 / [k_7 + k_8 + k_9] [k_4 + k_5 + k_6].$

If no triplet state is formed with CCl_3Br , then decomposition must occur from the lowest vibrational level S° of the excited singlet.

$$S^{\circ} \rightarrow CCl_{3^{\circ}} + Br_{\circ}$$
 (8')

In this case, eqn. (III) and (IV) remain unchanged, but ϕ_{∞} now has the definition $\phi_{\infty} = k'_{8}/(k_{4}+k_{5}+k'_{8})$.

The single stage mechanism (IV) implies a linear relationship between $\phi/(1-\phi)$ and $1/[CCl_3Br]$, while the multistage mechanism (VI) predicts a curve with slope

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increasing as $1/[CCl_3Br]$ increases. Both equations give an intercept of $\phi_{\infty}/(1-\phi_{\infty})$ at zero $1/[CCl_3Br]$.

Plots of $\phi/(1-\phi)$ against $1/[CCl_3Br]$ appear to be linear, but this is an insensitive test, particularly with CCl_3Br where wide pressure range data are experimentally inaccessible. Values of ϕ_{∞} , the high-pressure limit of the quantum yield, calculated from the intercept are given for each temperature in table 5.

Eqn. (III) and (IV) can be modified to (V) and (VI), which provide a more sensitive test, viz., from a plot of $(1 - \phi)/[CCl_3Br]$ against [CCl₃Br]:

$$\frac{1-\phi}{[\text{CCl}_3\text{Br}]} = \frac{1-\phi_{\infty}}{[\text{CCl}_3\text{Br}]} \prod_{i=1}^{n} \left[1/\left(1 + \frac{k_{2,i}}{k_{3,i}[\text{CCl}_3\text{Br}]}\right) \right]. \tag{V}$$

For single-stage deactivation

$$(1-\phi)/[\text{CCl}_3\text{Br}] = (1-\phi_\infty)/(k_2/k_3 + [\text{CCl}_3\text{Br}]).$$
 (VI)

Kutschke *et al.*¹¹ have shown that (VI) decreases smoothly from $(1-\phi_{\infty})/k_2/k_3$ at [CCl₃Br] = 0 to zero as [CCl₃Br] $\rightarrow \infty$, but that (V) will pass through a maximum



 \oplus , 90°; \triangle , 112°; ×, 147°; \bigcirc , 185°.

before decreasing to approach zero asymptotically. Fig. 1 shows the data plotted in this way. The curves all decrease smoothly as $[CCl_3Br] \rightarrow \infty$ and no maximum appears in the pressure range studied. As temperature increases the population of the higher vibrational levels of the excited state will be greater, and also $k_{2,i}/k_{3,i}$ will probably increase, so that the position of any maximum should move to higher pressures.¹¹ However, there is no sign of a maximum even at the highest temperature

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studied. The results cannot rule out a multistage deactivation process since they do not extend to the lowest pressures, but the absence of a maximum even at 185°, does imply that few of the excited singlet vibrational levels are involved. If we asume a strong deactivation mechanism, then the value of k_2/k_3 can be calculated at each temperature from the slopes of the $\phi/(1-\phi)$ lines. The values of ϕ_{∞} also shown in table 5 are independent of the deactivation mechanism chosen.

TABLE 5

temp. °C	ϕ_{∞}	$\frac{k_2/k_3}{k_2/k_3}$ single stage mechanism
90	0.014	1.63×10^{-5}
112	0.034	1.17×10^{-5}
147	0.187	1.85×10^{-5}
185	0.230	13.8×10^{-5}

Steps (4) and (7) represent fluorescence from the singlet and phosphorescence from the triplet. We have been unable to detect any fluorescence or phosphorescence emission from CCl_3Br with the rudimentary equipment available to us. Our apparatus is probably not sufficiently sensitive to detect a weak fluorescence. No reports of fluorescence from halo-methanes have appeared in the literature. This may therefore indicate that internal conversion (5) and intersystem crossing (9) are relatively important in this case.

EFFECT OF INERT GASES

The variation in the quantum yield ϕ , for various pressures of the inert gases CF₄ and CO₂, has been studied (table 4). For a fixed concentration of CCl₃Br, addition of inert gas lowers the quantum yield; this provides strong qualitative argument for the presence of a long-lived excited state. In the presence of an added inert gas N, a further series of steps must be added to the mechanism.

$$S^n + N \to S^{n-1} + N \tag{3',n}$$

$$T^{\circ} + \mathbf{N} \rightarrow \mathbf{CCl_3Br} + \mathbf{N} \tag{10}$$

or

$$S^{\circ} + N \rightarrow CCl_{3}Br + N.$$
 (10')

Steady state treatment leads to the expression

$$\frac{1-\phi}{[\operatorname{CCl}_3\operatorname{Br}]+[\operatorname{N}]} = \frac{1-\phi_{\infty}}{[\operatorname{CCl}_3\operatorname{Br}]+[\operatorname{N}]} \prod_{i=1}^{n} \left[1/\left(1+\frac{k_{2,i}}{k_{3,i}[\operatorname{CCl}_3\operatorname{Br}]+k'_{3,i}[\operatorname{N}]}\right) \right]$$
(VII)
where

$$\phi_{\infty} = k_6 k_8 / (k_7 + k_8 + k_9 + k_{10} [N]) (k_4 + k_5 + k_6).$$

If, however, we assume no triplet state participation, then reaction (10') supercedes, and $\phi_{\infty} = k'_8/(k_4+k_5+k'_8+k'_{10}[N])$. The function (VII) approaches zero asymptotically as $[N] \rightarrow 0$ and also

$$\lim_{[N]\to 0} \frac{1-\phi}{[\text{CCl}_3\text{Br}] + [N]} = (1-\phi_{\infty}) \prod_{i=1}^{n} \left[1/\left([\text{CCl}_3\text{Br}] + \frac{k_{2,i}}{k_{3,i}} \right) \right], \quad (V)$$

i.e., as the concentration of inert gas decreases the function approaches the value found for CCl₃Br alone. If $k'_{3,i} \leq k_{3,i}$, (VII) has no real maximum whatever the value of *n*. But if $k'_{3,i} > k_{3,i}$, then (VII) gives a maximum irrespective of the value of *n*.

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etc.

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With CF₄ and CO₂, $k'_{3,i} < k_{3,i}$. This is shown by plotting $\phi/(1-\phi)$ against 1/[N]; the gradient is much steeper when inert gas is used. No maximum can be expected in this case therefore. The plots of $(1-\phi)/[CCl_3Br]+[N]$ against total gas concentration are shown in fig. 2. The data are well represented by smooth curves tending towards a limit on the curve with CCl₃Br alone.



 \oplus , N = CO₂; ×, N = CF₄; O, CCl₃Br alone; temp. 147-148°.

CONCLUSIONS

The present results establish the participation of relatively long-lived electronically excited molecules in the photolysis of bromotrichloromethane at 3650 Å. The primary process in this photolysis is analogous to the photolysis of hexafluoroacetone¹³ or hexafluoroazomethane.¹⁴ In the absence of spectroscopic evidence, the nature of the excited state or states cannot be definitely established. The kinetic results imply that only a few vibrational levels of the electronically excited state are involved in collisional deactivation. As expected, the addition of a third body lowers the quantum yield. Both CF_4 and CO_2 are less efficient third bodies than CCl_3Br itself.

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