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STUDIES IN VACUUM ULTRA-VIOLET PHOTOLYSIS
PART V: THE PHOTOLYSIS OF CYCLOBUTANONE AT 147.0 nm AND 123.6 nm IN THE GAS PHASE


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Summary

The vacuum ultra-violet photolysis of cyclobutanone in the gas phase has been carried out at 147.0 and 123.6 nm. Two primary photochemical processes which produce vibrationally excited products have been shown to be important at these wavelengths:

$$\to CH_2CO^* + CH_2 = CH_2{}^* \qquad (1)$$

$$\to \cdot CH_2CH_2CH_2^* \cdot + CO \qquad (2)$$
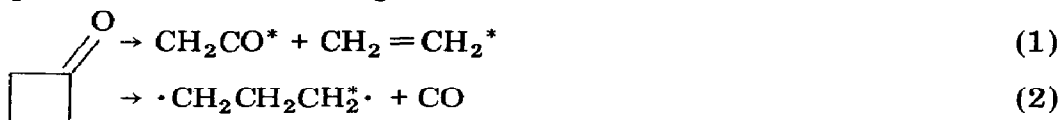
Radical processes are unimportant, the main reaction products arising either from the primary molecular reactions or subsequent isomerization or decomposition of vibrationally excited molecules. The ratio of the quantum yields of reactions (1) and (2) is a function of the wavelength of the exciting light and has a high pressure limiting value of 0.95 ± 0.05 and 0.45 ± 0.05 at 147.0 and 123.6 nm respectively. Detailed RRKM calculations have indicated that the cyclopropane molecule has, on average, 17 and 30 kJ/mol excess vibrational energy from the photochemical reactions at 147.0 and 123.6 nm respectively.

Fluorescence of electronically excited CO has not been observed and the implications of this fact are discussed.

Introduction

The photodecomposition of cyclobutanone (CB), both direct [1 - 11] and photosensitized [12, 13], has been extensively studied by a number of complementary techniques in the near ultra-violet. Studies of the benzene photosensitized decomposition [13] in the gas phase have clarified earlier suggestions concerning the roles played by the lowest triplet electronic state (T_1), the vibrationally excited ground electronic state (S_0^*) and the first excited electronic state (S_1^*). The latter work has indicated that ethylene and ketene arise from the decomposition of S_0^* whilst T_1 is a precursor of carbon

monoxide and vibrationally excited cyclopropane which isomerizes if not deactivated by prior collisional stabilization. On the basis of evidence derived from the fluorescence excitation spectroscopy of cyclobutanone [14], it is shown that a rapid predissociation process of the first excited singlet state accounts for most of the products arising from photolysis at wavelengths greater than 320 nm. Products formed from the triplet state (T_1) are only important near the threshold of the $S_0 \rightarrow S_1$ absorption band where $CB(S_1^*)$ has less than 12 kJ/mol excess vibrational energy. Propylene is formed as the isomerization product of the vibrationally excited cyclopropane, although the formation *via* a primary route during photolysis has not been entirely excluded.

A recent study [15] of the vacuum ultra-violet photolysis of cyclo-butanone has indicated that the primary modes of decomposition arise from states other than the first excited singlet and triplet states, whilst retaining an overall pattern of decomposition similar to the near ultra-violet decomposition. Evidence was presented for a primary route for the production of propylene at 147.0 nm which was absent at 123.6 nm and 106.7 - 4.8 nm. This was based, in part, on the observation that the ratio of propylene to cyclopropane increased as the energy of the exciting radiation decreased.

It is of importance to emphasize that, as a consequence of the production of energized products, new high energy chemical reaction pathways become available at room temperature for reactions conventionally studied at much higher temperatures. Photolysis in the vacuum ultra-violet allows the investigation of the rates of decomposition of molecules in highly excited states derived from the photofragmentation of the reactant molecule.

Experimental

Photolyses were carried out, at ambient temperatures, in a cylindrical Pyrex reaction vessel which was attached to a mercury-free, greaseless high vacuum system. Pressures better than 10^{-5} kN/m^2 were attained by means of a silicone oil diffusion pump backed by a two stage rotary oil pump. Reactant pressures were measured with a strain gauge pressure transducer which was calibrated with dry nitrogen against a silicone oil manometer. After irradiation, hydrocarbon product analysis was performed by gas chromatography employing a flame ionization detector. Sample injection was carried out using a stainless steel sampling valve, employing silicone rubber "O" ring seals, whose design precluded the use of grease.

Monochromatic light sources at 147.0 and 123.6 nm were provided by L-shaped rare gas resonance lamps powered by a 2450 megacycles/s microwave generator, with a LiF window affixed to the end of the discharge tube with a low pressure epoxy resin. The xenon lamp was operated with a cold finger using liquid oxygen refrigerant whilst the krypton lamp was held at liquid nitrogen temperatures.

TABLE 1

Hydrocarbon product distribution for photolysis at 147.0 and 123.6 nm of cyclobutanone

	Wavelength/nm	
	147.0[a]	123.6[b]
CH_4	0.1	0.1
C_2H_2	3.5	7.5
C_2H_4	100	100
C_3H_4	1.0	3.6
C_3H_6	5.1	17.5
$\triangle$	52.9	24.1
C_3H_8	0.5	0.1
c-t-butene-2	1.7	9.0

[a] Pressure of cyclobutanone 1.27 kN/m^2.
[b] Pressure of cyclobutanone 1.32 kN/m^2.

Cyclobutanone (Ralph N. Emanuel Ltd) was purified by trap-to-trap distillation until gas chromatographically pure and stored under vacuum at liquid nitrogen temperatures.

Conversions in all experiments were limited to less than 0.1%, and the chromatograph was calibrated for the major products of photolysis by injection of small, accurately determined pressures of the pure gases.

Results and Discussion

The hydrocarbon product distribution for photolysis at 147.0 and 123.6 nm at approximately 1.33 kN/m^2 of cyclobutanone is illustrated in Table 1. The high pressure limiting ratio of the quantum yields of processes (1) and (2) can be determined by extrapolation of the ratio $\Sigma C_3 / \Sigma C_2$ to infinite pressure as shown in Fig. 1 where this latter ratio is plotted as a function of the inverse of the cyclobutanone pressure for photolysis at 147.0 and 123.6 nm. The ratio of the quantum yields of reactions (1) and (2) is a function of the wavelength of the exciting radiation and has a high pressure limiting value of 0.95 ± 0.05 and 0.45 ± 0.05 at 147.0 and 123.6 nm respectively.

The photolysis of 1.99 kN/m^2 of cyclobutanone in the presence of 0.13 kN/m^2 of O_2 at 123.6 nm produced the following ratios: propylene/cyclopropane, 0.36; acetylene/ethylene, 0.08; cyclopropane/allene, 18.2. The minor saturated hydrocarbons were not formed under these conditions. Within the experimental error, the above ratios are equal to those found for photolyses carried out in the absence of O_2 at the same pressure.
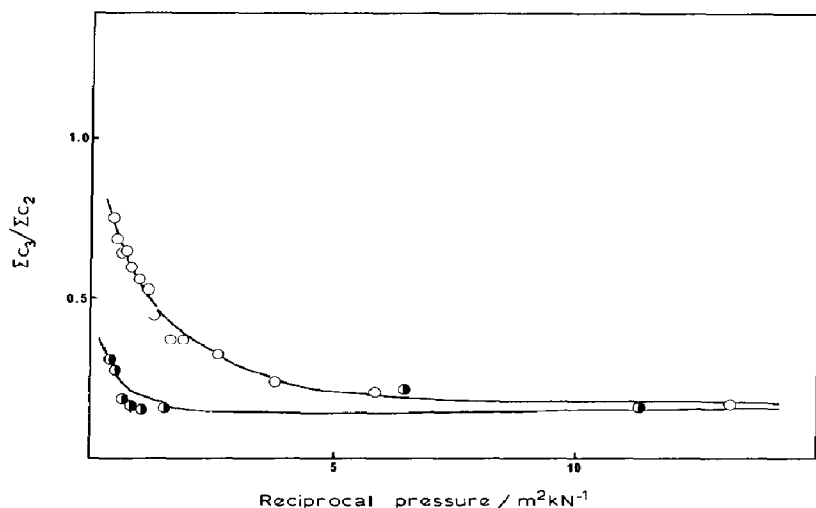
Fig. 1. Ratio of $\Sigma C_3/\Sigma C_2$ as a function of the reciprocal pressure, $1/P$, for photolysis of cyclobutanone at 147.0 nm (○) and 123.6 nm (◐).

The following mechanism, analogous to that proposed for the photolysis in the near ultra-violet, accounts for the major hydrocarbon products during the photolysis of cyclobutanone (CB) in the gas phase at 147.0 and 123.6 nm.

$$CB \rightarrow CH_2CO^* + C_2H_4^* \tag{1}$$

$$CB \rightarrow \cdot CH_2CH_2CH_2^* \cdot + CO \tag{2}$$

$$\cdot CH_2CH_2CH_2^* \cdot \rightleftharpoons c\text{-}C_3H_6^* \tag{3,-3}$$

$$\cdot CH_2CH_2CH_2^* \cdot \rightarrow C_3H_6 \tag{4}$$

$$c\text{-}C_3H_6^* + M \rightarrow c\text{-}C_3H_6 + M \tag{5}$$

$$C_2H_4^* + M \rightarrow C_2H_4 + M \tag{6}$$

$$c\text{-}C_3H_6^* \rightarrow C_3H_4 + H_2 \tag{7}$$

The variation of the propylene to cyclopropane ratio, Φ, with pressure is shown in Figs. 2 and 3 and suggests that the trimethylene biradical is a precursor to both compounds. This point is further illustrated by reference to Table 1 where the increase in the propylene/cyclopropane ratio with decreasing wavelength reflects the greater vibrational excitation of the trimethylene biradical.

The following rate equations can be derived on the basis of the steady state assumption:

$$\Phi = \frac{k_4}{k_3} + \frac{k_4}{k_3}\left(\frac{k_{-3} + k_7}{k_5 M}\right) \tag{A}$$
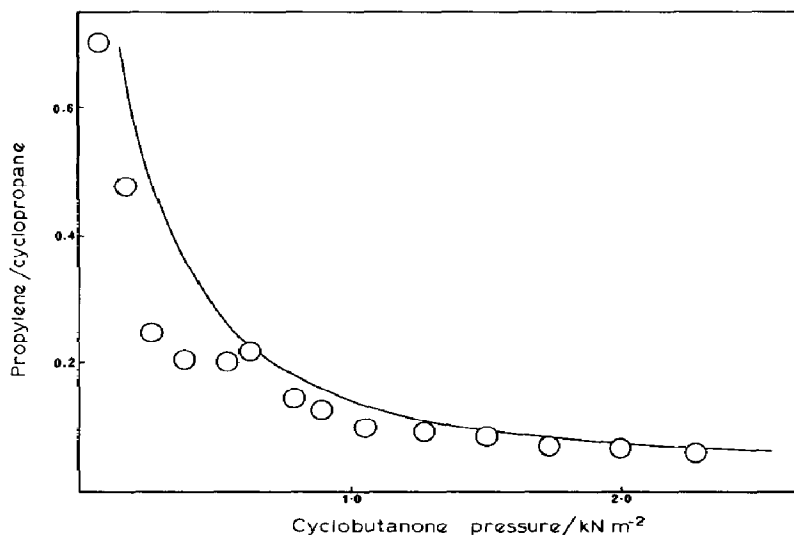
and

Fig. 2. Pressure dependence of propylene/cyclopropane ratio. Photolysis of cyclobutanone at 147.0 nm; —, theoretical curve.
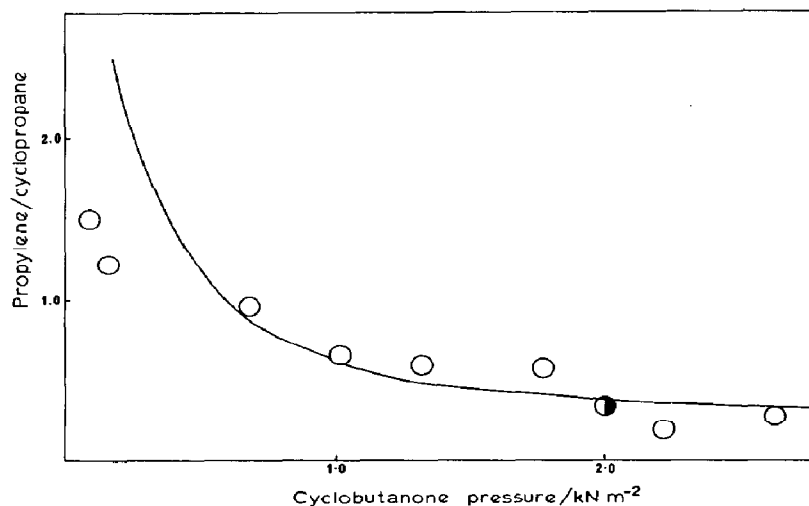

Fig. 3. Pressure dependence of propylene/cyclopropane ratio. Photolysis of cyclobutanone at 123.6 nm; —, theoretical curve; ◑, photolysis in presence of 0.13 kN/m^2 of O_2.

$$\frac{c\text{-}C_3H_6}{C_3H_4} = \frac{k_5\,M}{k_7} \qquad (B)$$

The ratio of propylene to cyclopropane is plotted in Fig. 5 as a function of the inverse cyclobutanone pressure: the form obtained is that required by the above expression. In addition, the linear dependence of the cyclopropane to allene ratio on the cyclobutanone pressure is illustrated in Fig. 4. Analysis of the data contained in Figs. 4 and 5 allowed the construction of Table 2.
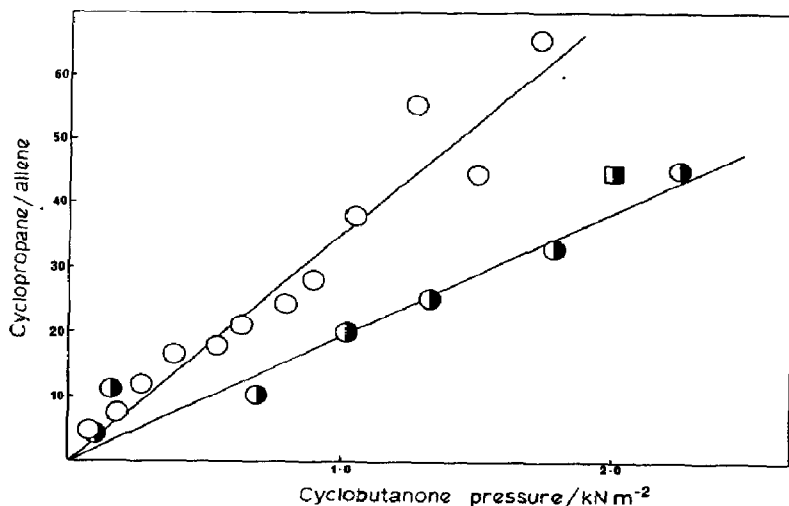
Fig. 4. Pressure dependence of cyclopropane/allene ratio for photolysis at 147.0 (○);
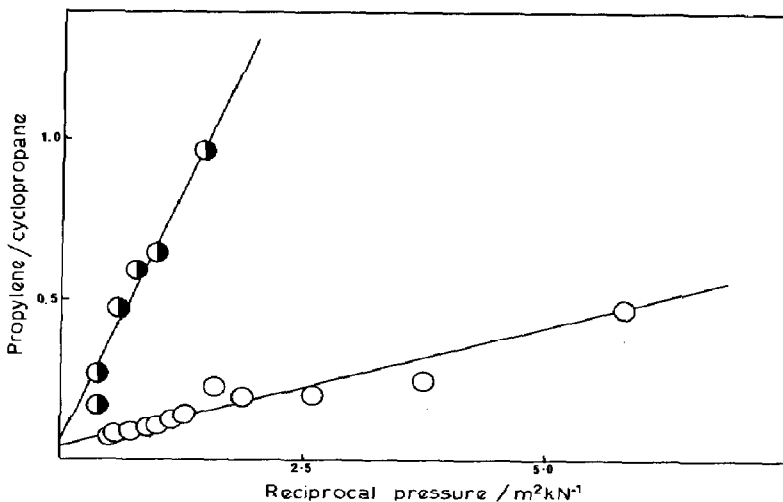◪, photolysis in presence of 0.13 kN/m^2 of O$_2$.

Fig. 5. The propylene/cyclopropane ratio as a function of the reciprocal pressure.
○, 147.0 nm; ◑, 123.6 nm.

The increase in the decomposition rates with decreasing photolysis wavelength in Table 1 reflects the greater vibrational excitation of the products, and points to allene formation from an excited primary product. The c-C$_3$H$_6$/C$_3$H$_4$ ratio would not show a simple linear relationship with pressure if allene were produced from the trimethylene biradical.

The following minor pathways, similar to those by Hampson *et al.* [16] to account for the formation of acetylene produced during the photolysis of ethane in the vacuum ultra-violet region, arise from the decomposition of excited ethylene:

$$C_2H_4^* \rightarrow C_2H_2 + H_2 \tag{8}$$
$$C_2H_4^* \rightarrow C_2H_2 + 2H \tag{9}$$

TABLE 2

Derived rate constants for elementary reactions

Photolysis wavelength/nm	Rate constant/s^{-1}		
	k_4/k_3	k_7	k_{-3}
147.0	5.0×10^{-2}	1.15×10^6	4.28×10^7
123.6	8.5×10^{-2}	4.91×10^6	3.01×10^8

k_5 calculated from simple kinetic theory 4.02×10^7 m^2 kN^{-1} s^{-1}.

Although the variation of acetylene to ethylene yields was not sufficient to provide accurate data for the levels of excitation of ethylene, the average value of the ratio of acetylene to ethylene can be used in conjunction with the specific rate constant [17] for the decomposition of excited ethylene by reaction (8) to compute the vibrational energy of $C_2H_4^*$.

The excess vibrational energy is 6.3 and 10.5 kJ/mol, which when combined with E_0 for reaction (8) provides values of 315.6 and 319.8 kJ/mol for the excitation energy of ethylene at 147.0 and 123.6 nm respectively. The total vibrational energy, assuming that it is distributed according to the number of degrees of vibrational freedom in ethylene and ketene, that arises in the products of reaction (1) at 147.0 nm is 553 kJ/mol which represents an energy loss, expressed as a fraction of the total available energy, of 0.32. This fractional energy loss, which increases to 0.42 for photolysis at 123.6 nm, suggests either rapid de-excitation of the initially populated higher electronic state or the intermediacy of a fragment which survives several collisions.

If the vibrationally excited cyclopropane arising from the photodissociation reaction has an energy distribution, $f(E)$, then the average rate constant, k_d, for the isomerization to propylene can be written [18] as:

$$k_d = w \int_0^\infty \frac{k_E}{k_E + w} f(E) \, dE \Big/ \int_0^\infty \frac{w}{k_E + w} f(E) \, dE \tag{C}$$

where k_E is the specific rate constant for the decomposition of cyclopropane at an excess vibrational energy E and w is the rate of deactivation of the energized cyclopropane.

The specific rate constant, k_E, was calculated from RRKM theory where $\Sigma P(E_v^{\ddagger})$ is the sum of the energy eigenstates of the active degrees of freedom for the complex at energy $E^{\ddagger}$, and

$$k_E = l^{\ddagger} \frac{\Sigma P(E_v^{\ddagger})}{hN^*(E)} \tag{D}$$

$N^*(E)$ is the density of energy eigenstates of the active degrees of freedom for the cyclopropane molecule at energy E, $l_v^{\ddagger}$ is the reaction path degeneracy. At values of $E^{\ddagger} \leqslant 100$ kJ/mol, $\Sigma P(E^{\ddagger})$ was calculated by a direct count method, and at energies above this, the energy level sum $\Sigma P(E_v^{\ddagger})$ and energy density $N^*(E)$ of the activated complex and active molecule respectively were

calculated by the approximation of Whitten and Rabinovitch [19]. At certain values of $E^{\ddagger} > 100$ kJ/mol, the above approximation was checked against the direct count method and the method of Hoare and Ruijgrok [20] and found to be reliable to within 1% error.

Neglecting the minor pathway to the formation of allene:

$$k_d = w \, \Phi \tag{E}$$

the average rate constant can be related to the measured propylene to cyclopropane ratio Φ by eqn. (C). The integration procedure was reduced to a summation over a small energy increment of 4.2 kJ/mol and a computer program was devised to perform the calculations. The summation was terminated at $E^{\ddagger} < 200$ kJ/mol. The addition of further terms produced a negligible effect on the final value of Φ. This latter ratio was unaffected by halving the energy increment. The energy distribution of the primary fragments arising from the absorption process is likely to be narrow owing to the monochromicity of the resonance radiation. The difficulty of an *a priori* calculation of the form of the total energy distribution made it necessary to employ a normal distribution to approximate $f(E)$. Variation of the energy distribution half-width had no marked effect on the calculated ratio in contrast to variation in the collisional deactivation rate. The rate of deactivation, w, was calculated by simple kinetic theory since there is evidence [21] to suggest that the strong collision assumption is valid under normal conditions.

The results of the calculations are illustrated in Fig. (2) and (3) where the solid line presents the data derived from expression (C) for photolyses at 147.0 and 123.6 nm respectively. The mean vibrational energy of the cyclopropane molecule has been adjusted in order to simulate the experimental results. It can be seen that there is a good correlation between the shape of the theoretical curves and the experimental results which points to the validity of both the calculations performed and the underlying mechanism. Thus, on comparison of the theoretical treatment with the experimental data, the average excess vibrational energy of cyclopropane is 17 and 30 kJ/mol from the photolysis at 147.0 and 123.6 nm respectively. The vibrational energy content of the cyclopropane, estimated, represents a fractional energy loss of 0.63 and 0.68 for photolysis at 147.0 and 123.6 nm respectively. The rate constant for the formation of an excited biradical from $CB(S_1^*)$ has a value $\geq 10^{10}$ s^{-1}, a value which if reflected in higher singlet states may perhaps suggest that energy loss can be accredited to simple collisional deactivation of a biradical intermediate.

The difference in the energy content of the primary products derived from Xe and Kr photolyses is less than 15 kJ/mol which is small compared to the difference in the excitation energy at the respective wavelengths.

It seems unlikely that the biradical intermediate arises directly from the initially populated state, but that internal conversion is responsible for the large energy loss observed in the primary processes.

Ketene formed in reaction (1) may be calculated to be sufficiently energetic to allow almost complete dissociation into methylene and carbon monoxide. In view of the large ratio of reactant to products, it can be stated unequivocally that the reaction of methylene with the products of the primary steps is only a very minor process. Secondary reactions of methylene with the products of reactions (1) and (2) would give rise to excited cyclopropane and methylcyclopropane.

The secondary reactions between methylene and the primary products increase in importance at low pressure. At the highest pressure employed in this study less than 10% of the initially formed methylcyclopropane would be collisionally stabilized [22] if the methylene were at thermal equilibrium. The isomerization of vibrationally excited methylcyclopropane arising from secondary reactions accounts for the formation of *cis*- and *trans*-but-2-ene during the photolysis. The product distribution after photolysis in the presence of oxygen indicates that 80% of the butene fraction is non-quenchable which reflects the mechanism of its formation suggested previously.

An increase in the yield of the outenes was observed in experiments performed at pressures less than 0.1 kN/m^2. This trend is clearly in line with the proposed mechanism of their formation and leads to the discrepancy between the observed propylene to cyclopropane ratio and theoretical prediction at pressures $< 0.5 \text{ kN/m}^2$.

The minor saturated products are formed from free radical reactions, demonstrated by the oxygen scavenging experiments, in which ethyl and propyl radicals arise from hydrogen atom addition to ethylene and propylene respectively. Previous studies of the photolysis of cyclic ketones in the vacuum ultra-violet indicate that a major percentage of the hydrogen formed in these systems arises from hydrogen atom combination. At low conversions, the main route of radical removal is hydrogen abstraction from cyclobutanone to form ethane and propane. The trace quantity of methane produced during the photolysis is entirely quenched on addition of oxygen, which clearly points to its formation *via* a radical mechanism. Methyl radicals may be produced either by the decomposition of excited propylene or by the subsequent decomposition of excited methylcyclopropane formed by the insertion of methylene into cyclopropane.

It has been established that the energy of the cyclopropane derived from photolysis has a total energy of 239 and 302 kJ/mol at wavelengths of 147.0 and 123.6 nm respectively. In view of the initial excitation energy of 813 kJ at 147.0 nm and 967 kJ at 123.6 nm, carbon monoxide may have a maximum excitation energy of 574 kJ and 665 kJ at the two wavelengths. This is sufficient, if the thermochemistry of this elementary reaction is considered, to produce the electronic states $a^3\pi$ and $a'^3\Sigma^+$ by the reaction:

$$\text{(cyclobutanone)} \longrightarrow \cdot CH_2CH_2CH_2\cdot^* + CO(a'^3\Sigma^+, a^3\pi)$$
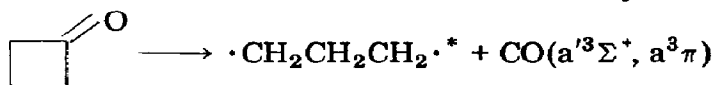
which, if a singlet trimethylene biradical is formed, is "spin allowed" only

if the cyclobutanone is in its triplet state. No fluorescence over the range 180 - 400 nm was observed during photolysis of 0.1 kN/m² of cyclobutanone at 123.6 nm.

The experimental observation of fluorescence from these states will depend on the relative magnitudes of the fluorescence lifetimes and collisional quenching rate constants. It has been shown [22] that the fluorescent lifetime for the process:

$$CO(a^3\pi) \rightarrow CO(X^1\Sigma^+) + h\nu$$

is very much longer than the collisional quenching lifetime and hence fluorescence from this transition would not be observed. In view of the possibility that the fluorescence lifetimes for the alternative processes may be of the same magnitude, no firm conclusions may be drawn as to the level of electronic excitation in carbon monoxide.

Acknowledgements

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