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Photolysis of trans-2,3-Dimethylcyclopentanone

By H. M. Frey,* Department of Chemistry, The University, Reading

D. H. Lister, Division of Pure Chemistry, National Research Council, Ottawa, Canada

The photolysis of *trans*-2,3-dimethylcyclopentanone has been investigated in the gas phase mainly at 3130 Å and 100°C. The major products of the decomposition are *cis*-2,3-dimethylcyclopentanone, *cis*- and *trans*-4-methylhex-4-enal, 2,3-dimethylpent-4-enal, *cis*- and *trans*-1,2-dimethylcyclobutane, *cis*- and *trans*-but-2-ene, ethylene, and carbon monoxide. These products are consistent with the formation of biradical intermediates. The variations of the product ratios have been measured as a function of pressure, temperature, wavelength, and added gases. Quantum yields for the various modes of decomposition have been determined over the pressure range studied. Benzene-photosensitised decompositions and liquid-phase photolyses in presence and absence of penta-1,3-diene, combined with a reinterpretation of previous data for cyclopentanone, favour the intermediacy of the triplet state in the decomposition of cyclopentanones.

By analogy with the simple aliphatic ketones, Benson and Kistiakowsky¹ and Blacet and Miller² suggested that the photolytic decomposition of cycloalkanones proceeded by a biradical mechanism. Srinivasan,³ however, preferred to explain the observed data, from photolyses of methyl-substituted cycloalkanones and photolyses in presence of oxygen, by a concerted stereospecific

¹ S. W. Benson and G. B. Kistiakowsky, J. Amer. Chem. Soc., 1942, **64**, 80.

mechanism. He suggested that decomposition occurred from the excited singlet state and that the nature of the product was determined by the vibrational energy of the excited molecule at the instant of decomposition. Srinivasan also suggested that the photolysis of a suitably substituted cycloalkanone, *e.g.*, *cis*- or *trans*-2,3-dimethylcyclopentanone, might distinguish between

² F. E. Blacet and A. Miller, J. Amer. Chem. Soc., 1957, 79, 4327.

³ R. Srinivasan, Adv. Photochem., 1963, 1, 83.

J. Chem. Soc. (A), 1970

the mechanistic choices. Pritchard et al.⁴ have photolysed cis- and trans-2,6-dimethylcyclohexanone and found that either isomer gave the same major products and in the same ratios: this was interpreted in terms of biradical intermediates. Lee,⁵ applying the benzenephotosensitisation technique to cyclopentanone and [2-3H1]cyclopentanone, has identified the formation of aldehydes with the triplet state. The present work has attempted to clarify the paths by which decomposition occurs.

EXPERIMENTAL

Apparatus.—A conventional high-vacuum gas-handling system was used with a cylindrical quartz reaction cell (5 cm. diam. and 10 cm. long), maintained at the desired temperature in an air furnace. The pressure in the reaction cell was measured with a glass spiral Bourdon gauge. All parts of the system in contact with the reactant or photolysis mixtures were fitted with Springham greaseless taps (Viton A diaphragms) and heated to 100° by Electrothermal tape to minimise absorption. Except when required for a run, the reactant was kept frozen in a cold finger immersed in an acetone-solid CO₂ bath. The light source was a super-pressure mercury arc (Wotan HBO 200 w), either filtered with a 4 mm. thick Pyrex disc, or in conjunction with a Bausch and Lomb high-intensity grating monochromator. The monochromator slits used resulted in 'monochromatic' light of a bandwidth of ca. 100 Å. The unilluminated volume of the reaction cell was less than 5%of the total. Light intensities were monitored by a phototube, the output of which was fed to the input of a Perkin-Elmer model F.11 flame ionisation amplifier and its output, suitably attenuated, was displayed on a potentiometric recorder.

Analysis was by gas chromatography on a Perkin-Elmer model F.11 instrument fitted with a gas sampling valve. An all-glass sample loop was used instead of the usual stainless steel loop, as this avoided problems associated with adsorption of carbonyl compounds on metal surfaces.⁶ The whole injection system was heated to 100°. Two columns were used to analyse the products completely: (a) 18 ft. $\times \frac{1}{8}$ in. containing 25% (w/w) polypropylene glycol on 60-80 mesh Chromosorb P resolved all the hydrocarbon products: (b) 10 ft. $\times \frac{1}{8}$ in. containing 20% (w/w) fluorosilicone oil (Perkin-Elmer FS1265) on 80-100 mesh Chromosorb W (HMDS treated) gave an excellent separation of all products except cis- and trans-but-2-ene. To obtain both reasonable resolution and acceptable retention times, analyses on both columns involved changes, made manually, in temperature and pressure during analysis. Calibration factors for the detector response to the different products were determined by analysis of known mixtures under the conditions used for analysis of the reaction mixtures.

Materials and Identification of Products.--Commercial 2,3-dimethylcyclopentanone was shown by g.l.c. to be 97% trans with 3% of the cis-isomer. Preparative g.l.c. rendered the trans-2,3-dimethylcyclopentanone 99.8% pure, the impurity being the cis-isomer. Benzene and acetone were Fison's analytical grade reagents, used without purification.

⁴ R. L. Alumbaugh, G. O. Pritchard, and B. Rickborn, J. Phys. Chem., 1965, 69, 3225.
 ⁶ E. K. C. Lee, J. Phys. Chem., 1967, 71, 2804.
 ⁶ D. C. Montague, Ph.D. Thesis, Southampton University,

1967.

Commercial grade penta-1,3-diene was treated with maleic anhydride to remove the trans-penta-1,3-diene and to leave the cis-isomer. Preparative g.l.c. then gave the pure cisisomer. Oxygen and oxygen-free nitrogen were from British Oxygen Co. The lower hydrocarbons were Matheson products and the cis- and trans-1,3-dimethylcyclobutanes were supplied by W. D. Walters. The aldehydes were synthesised by the method of Watanabe and Conlon.⁷

The hydrocarbons and aldehydes were identified by comparison of their g.l.c. retention times on several columns with those of authentic samples. The only other chromatographic product peak, when isolated by preparative g.l.c., gave i.r., n.m.r., and mass spectra differing only in minor detail from those obtained from trans-2,3-dimethylcyclopentanone. On this evidence it was assigned as cis-2,3dimethylcyclopentanone.

RESULTS

From mass balance measurements, the modes of decomposition shown in Scheme 1 are suggested for trans-2,3-di-



methylcyclopentanone. For cyclopentanone the relationship (1) holds for wide ranges of temperatures, pressure, and

$$CO = \frac{1}{2}C_2H_4 + C_4H_8$$
 (1)

wavelength.^{2,3,8} In the present study, analyses for CO were not performed and CO was estimated from equation (2). At 100° and during times much longer than those

$$CO = C_4 H_8 + C_6 H_{12}$$
(2)

used in photolyses, no ' dark ' reaction of trans-2,3-dimethylcyclopentanone (trans-2,3-DMCP) was observable. The majority of photolyses were for 4 hr. which gave 1-2% total decomposition. In initial experiments the ratio of the butenes to 1,2-dimethylcyclobutanes decreased (for ca. 40 photolyses) from values of ca. 3.3 to a final reproducible value of 1.5 which is in good agreement with that found

8 R. F. Klemm, D. N. Morrison, P. Gilderson, and A. T. Blades, Canad. J. Chem., 1965, 43, 1934.

⁷ W. H. Watanabe and L. E. Conlon, J. Amer. Chem. Soc., 1957, **79**, 2828.



FIGURE 1 (a) Variation of hydrocarbon ratios with pressure. (\bigcirc Pure ketone, \bigcirc with added nitrogen), A trans-but-2-ene : cisbut-2-ene, B trans-2-methylcyclobutane : cis-2-methylcyclobutane, and C C₄H₈ : C₆H₁₂; (b) variation of aldehyde ratios A and B with pressure (see Table 1 for definitions); (c) variation of the ratio R·CHO : CO with pressure

earlier.⁹ No reason for this decrease was found, though it may have resulted from active sites on the new cell surface which were slowly destroyed. Also variations of all *trans*: *cis* ratios, especially of but-2-ene, were noted if the injectionblock temperature of the chromatograph was above *ca*. 150°. Heterogeneous isomerisation on the hot metal surface was almost certainly the cause of this. Normally the injection block was at 100° and checked periodically with a thermocouple. Analysis for *cis*-2,3-dimethylcyclopentanone (*cis*-2,3-DMCP) was the least accurate since the peak was incompletely resolved from the peak for the reactant and large corrections always had to be made. Table 1 shows the result obtained for photolyses carried to varied extents of decomposition. For this series, the light source



FIGURE 2 Beer-Lambert plot for A, acetone, and B, trans-2,3-dimethylcyclopentanone at 100° and 3130 \pm 50 Å

was used with the 4 mm. thick Pyrex disc as filter. Although scatter is evident, the constant hydrocarbon : aldehyde ratio and the absence of extra peaks at high percentage decomposition indicates that the secondary decomposition of the aldehydes is negligible.

Further runs [Figure 1(a)—(c)], with various initial pressures, showed that the major effect of pressure change was to alter the aldehyde: CO ratio. (Nitrogen gas was used to extend the pressure range and its collisonal efficiency was estimated to be 0.17 that of the reactant.) Two other pressure effects were noted: (a) the decrease in the *trans*: *cis*-but-2-ene ratio below *ca*. 10 mm.; (b) the *cis*: trans-4-methylhex-4-enal ratio variation over the whole pressure range studied.

Product quantum yields were determined by acetone actinometry. Beer-Lambert plots of the logarithm of the light intensity against ketone pressure gave good straight lines (Figure 2), from which molar extinction coefficients were calculated by the method of least squares, whence ε (acetone) = 3.361. mole⁻¹ cm.⁻¹ and ε (trans-2,3-DMCP) = 9.461. mole⁻¹ cm.⁻¹ at 100° and 3130 \pm 50 Å. The pressuredependence of the product quantum yield is shown in Figure 3. As *cis*-2,3-dimethylcyclopentanone is an observable product, it is a reasonable assumption that *trans*-2,3-dimethylcyclopentanone is re-formed. Since this is not observable, the measured total product quantum yield will be less than unity. This could account for the total

⁹ H. M. Frey, Chem. and Ind., 1966, 947.

		Pressure =	8.0 mm. $\lambda = ca.3$	100 A. $T =$	= 100°		
	Decomp.	trans-Butene	trans-C4H6Me2 *	C_4H_8	Ratio	Ratio	CO †
Run	(%)	cis-Butene	cis-C4H6Me2	$\overline{C_6H_{12}}$	A	B	R ·CHO
91	1.0	4 ·26	2.03	1.55	1.86	10.61	3.88
73	3.3	3.92	$2 \cdot 20$	1.57	1.90	9.00	4.27
85	5.0	4.22	2.15	1.55	1.85	10.28	
63	6.3	3.97	2.06	1.43			
67	6.3		2.14	1.59	1.88	9.89	
88	6.3	4.02	2.02	1.51	1.77	9.00	3.86
71	8.3	4.20	2.08	1.63	1.89		
74	10.0	3.92	2.16	1.67	1.88	8.68	4.26
82	10.0	4.15	$2 \cdot 20$	1.60	1.86	10.74	3.17
86	13.3	4.26	2.07	1.56	1.87	10.04	3.83
77	15.0		2.04	1.57	1.83	8.83	4.33
81	20.0	4.04	2.06	1.54	1.86	9.75	3.34
76	30.0		2.04	1.59	1.83	8.74	4.42
83	30.0	4.18	2.08	1.59	1.88	10.92	3.67

TABLE 1

Ratio A = trans-4-methylhex-4-enal: cis-4-methylhex-4-enal. Ratio B = (trans- + cis-4-methylhex-4-enal): 2,3-dimethyl-pent-4-enal.

* 1,2-Dimethylcyclobutanes. † Uncalibrated.

				TABLE 2					
	λ	P	trans-Butene	cis-C4H6Me2 *	C_2H_4	C_4H_8	Ratio	Ratio	R.CHO
remp.	(Å)	(mm.)	cis-Butene	trans-C4H6Me2	C4H8	C_6H_{12}	\boldsymbol{A}	B	CO
100°	3130	8.1	3.97	2.00	1.00	1.56	1.85	9.27	0.521
153	3130	$7 \cdot 2$	3.87	1.85	1.00	1.54	1.72	11.55	0.243
159	3130	3.0	4.18	2.00	1.00	1.60	1.70	10.43	0.212
159	3130	8.0	4.34	1.89	1.00	1.62	1.78	10.50	0.238
100	2800	8.0	3.77	1.98	1.00	1.55	1.82	9 ·00	0.083

* 2,3-Dimethylcyclobutanes.

product quantum yield's being less than unity even with negligible fluorescence and phosphorescence yields.

Photolyses at other temperatures and wavelength showed that the aldehyde: CO ratio was sensitive to both these factors (Table 2).

As tests for radical intermediates or triplet-state participation, mixtures of trans-2,3-dimethylcyclopentanone with oxygen or *cis*-penta-1,3-diene (in gas and liquid phases)



FIGURE 3 Pressure-dependence of quantum yields (ϕ). A, Quantum yield for decomposition, ϕ Decomp.; B, ϕ trans-2,3-dimethylcyclopentanone; C, ϕ cis-2,3-dimethylcyclopentanone; D, ϕ R·CHO; and E, ϕ CO

were photolysed. Oxygen pressures up to only 5 mm, were used and although there was no change in product ratios, new peaks presumably corresponding to photo-oxidation products, appeared on the chromatographic traces. With cis-penta-1,3-diene (up to 200 mm.) a small reduction in the quantum yield of carbonyl products was found but the effect was scarcely outside experimental error. In the liquid phase, three solutions in Pyrex vessels were photolysed with a medium-pressure mercury arc lamp: (a) 2%trans-2,3-DMCP in cyclohexane, (b) 2% trans-2,3-DMCP and 2% cis-penta-1,3-diene in cyclohexane, (c) 2% trans-2,3-DMCP in a 1:1 mixture of penta-1,3-diene-cyclohexane. In (a) the only products were cis- and trans-4-methylhex-4-enal, 2,3-dimethylpent-4-enal, and cis-2,3-dimethylcyclopentanone; (b) showed that the yields of all these products were significantly reduced, while (c) resulted in almost complete quenching of the products [yield < 10% of that found in (a)]. cis-trans-Isomerisation of cis-penta-1,3-diene also occurred.

Benzene-photosensitised decompositions (Table 3) gave large quantities of aldehydes. In direct photolysis at these wavelengths no aldehyde was detected.

TABLE 3								
λ (Å)	P (Ketone) (mm.)	$P (C_6 H_6)$ (mm.)	$\stackrel{\textbf{Ratio}}{A}$	$\underset{B}{\textbf{Ratio}}$	$\frac{R \cdot CHO}{CO}$			
2470	10.0	10.0	2.00	10.94	0.380			
2530	10.0	10.0	2.01	1 6·60	0.405			
2530	1.0	5.0	2.00		2.04			
2530	10.0	0.0			$<\!0.02$			

Photolyses with a mercury resonance lamp gave only hydrocarbon products. Under these conditions the decomposition was shown to be mercury-photosensitised since by photolysing the ketone in presence of a large excess of

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nitrous oxide, the yield of products was substantially reduced (Table 4).

During the purification of trans-2,3-dimethylcyclopentanone, the cis-isomer was also trapped out. Analysis showed it to be 40% cis: 60% trans-isomer. Photolysis at 3130 Å of this sample gave, within experimental error, the same values for the hydrocarbon and aldehyde cis: trans ratios as obtained from the pure trans-2,3-dimethylcyclopentanone. However ratio B and the CO: aldehyde ratio were both higher by a factor of ca. 2.

DISCUSSION

The lack of stereospecificity of the products strongly suggests biradical intermediates, *i.e.*, Scheme 2. The



acyl-alkyl biradicals can either ring-close to re-form the cyclic ketone, internally abstract hydrogen to form presence of the triplet state ¹³ in liquid-phase photolyses. The conclusions from gas-phase benzene-photosensitised decompositions of cyclopentanone and [2-3H1]cyclopentanone⁵ and also from trans-2,3-dimethylcyclopentanone argue that the triplet state is the precursor of aldehydes in the gas phase as well.

Contrary to Srinivasan's conclusions,¹⁴ the data for photolyses of cyclopentanone with oxygen do not rule out the triplet state. Comparison of oxygen and methane as added gases shows that while the yields of ethylene and cyclobutane are identical for both gases, the pentenal yield in the presence of oxygen is half that in the presence of methane. Also, the pentenal decrease is paralleled by the mass-balance decrease. Although oxygen is known to quench excited singlet states 15 the absence of quenching of hydrocarbons and the extent of quenching of pentenal can be interpreted as evidence for a short-lived triplet state's being the pentenal precursor. Likewise with 2,6-dimethylcyclohexanone,⁴ the hydrocarbon : aldehyde ratios in the photolyses with oxygen present, are higher than the values predicted for comparable pressures of pure ketone-inert

P (Ketone)	Photolysis time (min.)	trans-Butene	$\frac{trans-C_4H_6Me_2}{cis-C_4H_6Me_2}$	$\frac{C_2H_4}{C_4H_8}$	$\frac{C_4H_8}{C_6H_{12}}$	CO (%)	R·CHO (%)	cis-2,3- DMCP (%)
5.2 4	3.0	3.04	1.92	1.02	1.64	0.45	0.0	0.0
5.50	3.0	3.11	1.79	1.00	1.61	0.75	0.0	0.0
5.0 .	3.0		1.87	1.00	1.64	0.13	0.0	0.0
		$P_{\mathrm{Hg}} = ca.\ 2\ imes\ 10^{-3}$	mm. $^{b} P_{Hg} = ca.$	0·2 mm.	• +35 mm. 1	N ₂ O.		

TABLE 4

unsaturated aldehydes, or decarbonylate to the substituted tetramethylene biradical, which itself may close to give 1,2-dimethylcyclobutanes or cleave to ethylene and but-2-enes.

The quantity most sensitive to the energy content of the excited molecule is the aldehyde: hydrocarbon (or CO) ratio. The results of varying pressure, frequency, or temperatures are consistent with the hydrocarbons being formed by a relatively higher energy pathway. Other data ¹⁰ indicate that the bond dissociation energy for RCO \longrightarrow R + CO is ca. 10 kcal. mole⁻¹, while the activation energy for hydrogen abstraction is probably ca. 2-4 kcal. mole⁻¹. From limited data at three temperatures, it appears that $E_{\rm CO} - E_{\rm RCHO} = ca. 4.5$ kcal. mole⁻¹ and $\log A_{\rm RCHO} - \log A_{\rm CO} = 2.9$.

In agreement with this energy-dependence, the liquidphase results, though not necessarily comparable, show that only aldehydes and *cis*- (and presumably *trans*)-2,3-dimethylcyclopentanone are formed. These products can be quenched by penta-1,3-diene, which undergoes cis-trans isomerisation. Photolyses 11 and radiolyses ^{11,12} of liquid cyclopentanone have shown that at least 70% of the product pent-4-enal can be quenched by penta-1,3-diene. These results clearly infer the

¹² D. L. Dugle and G. R. Freeman, Trans. Faraday Soc., 1965, **61**, 1174.

gas and indicate that the same quenching process is occurring.

Further quenching data are needed before the singlet state can be excluded as a source of the carbonyl products. Also we know from quantum yields for CO that the hydrocarbon precursor can be collisionally deactivated even at the lowest pressures used (1.5 mm.). Therefore if the precursor is a triplet species (and is also presumably the precursor of the aldehydes) then an effect with oxygen similar to that found with the aldehydes might have been expected. If it is a singlet, then no oxygen quenching would be expected. Thus a possible explanation for the absence of quenching is that the hydrocarbons formed in the photolysis of cyclopentanones arise directly by a singlet pathway. The mechanism in Scheme 3 is suggested for the photodecomposition of trans-2,3-dimethylcyclopentanone.

The first excited singlet and triplet states are represented by S and T respectively, and the vibrational level within the state by a subscript. Only two vibrational levels of the singlet and one of the triplet are shown although many are probably involved.

For simplicity the aldehydes are collectively represented as R·CHO, since their ratios vary only slightly with experimental parameters. Also, the invariance of 13 G. S. Hammond, N. J. Turro, and P. A. Leermakers, $\boldsymbol{J}\boldsymbol{.}$

¹⁰ J. A. Kerr, Chem. Rev., 1966, 66, 465.

¹¹ P. Dunion and C. N. Trumbore, J. Amer. Chem. Soc., 1965, 87, 4211.

Phys. Chem., 1962, 66, 1144.
 ¹⁴ R. Srinivasan, J. Amer. Chem. Soc., 1961, 83, 4344.
 ¹⁵ W. R. Ware and S. K. Lee, to be published.

the but-2-ene: 1,2-dimethylcyclobutane ratio implies that these hydrocarbons have a common precursor, namely the substituted tetramethylene biradical. As the only reaction of this species is to form hydrocarbons, the process (3) can be condensed to (4). Campbell and

$$\begin{array}{cccc} trans-2,3\text{-DMCP} + h\nu & \longrightarrow & \mathbf{S_a} & & I_a \\ & & \mathbf{S_a} & \longrightarrow & \text{hydrocarbons} + \text{CO} & & k_2 \\ & & \mathbf{S_a} & \longrightarrow & \mathbf{T} & & k_3 \\ & & \mathbf{M} + \mathbf{S_a} & \longrightarrow & \mathbf{S_0} + (\mathbf{M}) & & k_4 \\ & & \mathbf{T} & \longrightarrow & \mathbf{RCHO} & & k_5 \\ & & & \mathbf{T} & \longrightarrow & \mathbf{RCHO} & & k_6 \\ & & & & \mathbf{T} & \longrightarrow & \mathbf{rcas}-2,3\text{-DMCP} & & k_7 \\ & & & & \mathbf{S_0} & \longrightarrow & \mathbf{hydrocarbons} + \mathbf{CO} & & k_8 \\ & & & & \mathbf{S_0} & \longrightarrow & \mathbf{T} & & & k_9 \\ & & & & \mathbf{S_0} & \longrightarrow & \mathbf{trans}-2,3\text{-DMCP} & & k_7 \\ & & & & & \mathbf{S_0} & \longrightarrow & \mathbf{T} & & & k_9 \\ & & & & & \mathbf{S_0} & \longrightarrow & \mathbf{trans}-2,3\text{-DMCP} & & k_7 \\ & & & & & & \mathbf{S_0} & \longrightarrow & \mathbf{T} & & & k_9 \\ & & & & & & \mathbf{S_0} & \longrightarrow & \mathbf{trans}-2,3\text{-DMCP} & & & k_8 \\ & & & & & & \mathbf{S_0} & \longrightarrow & \mathbf{T} & & & & k_9 \\ & & & & & & \mathbf{S_0} & \longrightarrow & \mathbf{trans}-2,3\text{-DMCP} & & & k_1 \\ & & & & & & & \mathbf{S_0} & \longrightarrow & \mathbf{T} & & & & \mathbf{S_0} \\ & & & & & & & \mathbf{S_0} & \longrightarrow & \mathbf{T} & & & & \mathbf{S_0} \\ & & & & & & & \mathbf{S_0} & \longrightarrow & \mathbf{T} & & & & \mathbf{S_0} \\ & & & & & & & \mathbf{S_0} & \longrightarrow & \mathbf{T} & & & & \mathbf{S_0} \\ & & & & & & & \mathbf{S_0} & \longrightarrow & \mathbf{T} & & & & \mathbf{S_0} \\ & & & & & & & \mathbf{S_0} & \longrightarrow & \mathbf{T} & & & \mathbf{S_0} \\ & & & & & & & \mathbf{S_0} & \longrightarrow & \mathbf{T} & & & \mathbf{S_0} \\ \end{array}$$

Schlag¹⁶ have shown that for similar photolytic decompositions statistical arguments for predicting the energy distribution of products are questionable. If

$$S_{a} \longrightarrow (3)$$

$$S_{a} \longrightarrow hydrocarbons + CO$$

this is true for cyclopentanones, we have little idea of the energy content of the hydrocarbon precursor. From the pyrolysis of *cis*-1,2-dimethylcyclobutane ¹⁷ we infer that the $C_2 + C_4$ hydrocarbons are formed by an independent pathway and not from a 'hot' 1,2-dimethylcyclobutane molecule (the latter is thought to occur at very low pressures in the case of cyclopentanone⁸). Photolysis of 2,2,5,5-tetradeuteriocyclopentanone³ leads to identical conclusions.

Emission studies ¹⁸ have shown that cyclopentanone exhibits weak fluorescence in all phases and that its efficiency in the gas phase is pressure-independent. No phosphorescence was observed in the gas phase. By analogy, a pressure-independent term is included in Scheme 3 and when absolute values of fluorescence efficiency are available we can decide if this process is negligible.

As the hydrocarbons are formed by the higher energy pathway, the rate of their formation will be more sensitive to the vibrational energy of the excited molecule. At 3130 Å, this energy is probably *ca.* 15 kcal. mole⁻¹ and we may assume that $k_2 \gg k_8 \ll k_9$. A mathematical analysis of the mechanism, with the usual steady-state assumptions, gives equation (5). Graphically [Figure 1(c)] the linear plot justifies the assumption used $(k_2 \gg k_8)$.

$$\frac{[\text{R}\cdot\text{CHO}]}{[\text{CO}]} = \frac{1}{k_2} \cdot \frac{k_5}{k_5 + k_6 + k_7} \cdot \left[k_3 + \frac{k_4 k_9 [\text{M}]}{k_8 + k_9 + k_f} \right]$$
(5)

The derived quantum yield expressions predict equation (6) from which (Figure 4) $k_3/k_2 = 2 \cdot 1$ (*i.e.* at 3130 Å

$$\frac{1}{\phi CO} = 1 + \frac{k_3}{k_2} + \frac{k_4}{k_2} [M]$$
(6)

the rates of intersystem crossing and decomposition from the highest vibrational level are comparable) and $k_4/k_2 = 0.113$ torr⁻¹. To a first approximation, we can equate the deactivation rate constant k_4 to the standard collision number (= 7.7×10^6 torr⁻¹ sec.⁻¹ at 373° k with a molecular weight of 112 and a collision diameter of 5 Å), and hence $k_2 = 6.8 \times 10^7$ sec.⁻¹ and $k_3 = 1.4 \times 10^8$ sec.⁻¹.



FIGURE 4 Pressure-dependence of $1/\phi$ CO

The relations for *cis*- and *trans*-2,3-dimethylcyclopentanone and aldehydes are all of the form (7) and

$$\phi_{x} = \frac{k_{x}}{k_{5} + k_{6} + k_{7}} \cdot \left[k_{3} + \frac{k_{4}k_{9}[M]}{k_{8} + k_{9} + k_{f}} \right] \cdot \frac{1}{k_{2} + k_{3} + k_{4}[M]} \quad (7)$$

predict that a constant value should be reached at high pressures. Experimentally [Figure 3) results are not available for high enough pressures to know whether a limit is reached, (ϕ trans-2,3-DMCP is taken as $1 - \phi$ Decomp. and will only be true if k_t is negligible). The slight decrease in the plot for ϕ cis-2,3-DMCP is almost certainly due to a systematic overcorrection in the analysis and a small positive slope is more likely correct. Also, the relation predicts a constant ratio for any two of the three. However, the ratio of cis-2,3-DMCP to RCHO changes from 1.86 (P < 30 mm.) to 1.3 at 130 mm. and is only 0.95 in the liquid phase. The reason for this decrease is not clear, but the formation of the

¹⁶ R. J. Campbell and E. W. Schlag, *J. Amer. Chem. Soc.*, 1969, **89**, 5103.

¹⁷ H. R. Gerberich and W. D. Walters, J. Amer. Chem. Soc., 1961, **83**, 3935.

¹⁸ S. R. LaPaglia and B. C. Roquitte, J. Phys. Chem., 1962, **66**, 1739; Canad. J. Chem., 1963, **41**, 287.

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aldehydes may be favoured energetically over formation of the ketones.

Above 30 mm., the ratios of cis-2,3-dimethylcyclopentanone to *trans*-4-methylhex-4-enal and of trans-2,3-dimethylcyclopentanone to *cis*-4-methylhex-4-enal and 2,3-dimethylpent-4-enal are very similar and only decrease slowly with increasing pressure (Table 5) (the

TABLE 5								
Pressure (mm.)	$2 \cdot 2$	8.1	20.0	31.0	52	102	136	
Ratio 1 Ratio 2	0·597 0·575	$0.561 \\ 0.516$	$0.546 \\ 0.521$	$0.583 \\ 0.543$	$0.540 \\ 0.538$	$0.480 \\ 0.494$	$0.449 \\ 0.458$	

last term in the second ratio is necessary since *trans*-2,3-dimethylcyclopentanone can arise from either of the biradicals formed initially by C(1)-C(2) or C(5)-C(1) bond fission). This probably indicates that each ketonealdehyde pair has a common precursor. Also the pressure variation of the *trans*: *cis*-2,3-dimethylcyclopentanone ratio (Figure 5) is, within experimental limits,



FIGURE 5 Pressure-dependence of the ratio trans : cis-2,3-dimethylcyclopentanone

the same as for the cis: trans-4-methylhex-4-enal ratio: less than 5% error in cis-2,3-dimethylcyclopentanone analysis accounts for the discrepancy. If these correlations are not fortuitous then it appears that aldehyde and ketone are formed from the same electronic energy level.

These observations are consistent with an energydependent equilibrium between the two configurations of the biradical which lead to products. At high internal energies we would expect the frequency of rotation of the penultimate bond [originally the C(2)-C(3) bond] to be such that collisional de-excitation to form product molecules in their ground electronic state is equally likely for both configurations. At low internal energies, the rate of rotation will be lower and the time spent in a particular configuration (*i.e.*, the chance of forming a particular pair of products) will be determined by the rotational activation barriers and the enthalpy difference between the two configurations. Thus a pressuredependence of the aldehyde and ketone ratios is expected [Figures 1(b) and 5]. If the high-pressure limit of these ratios is <2.5 then the free energy difference between the lowest vibrational levels of the biradical configurations is <680 cal. mole⁻¹. These arguments imply that several vibrational levels of the triplet state are involved. A similar energy-dependence of the substituted tetramethylene biradical accounts for the drop in the *trans*: *cis*-but-2-ene ratio below 10 mm.

If we assume that a constant *trans*: *cis*-ratio indicates that all the excited molecules have been deactivated to the lowest vibrational level, then the pressure at which the ratio becomes constant gives a measure of the lifetime of the precursor. Thus the lifetimes of the precursors of the but-2-enes and aldehydes, *i.e.*, the singlet and triplet states of *trans*-2,3-dimethylcyclopentanone are 1.3×10^{-8} sec. and $<1 \times 10^{-9}$ sec. respectively.

On the basis of the mechanism presented the results of the mercury-photosensitised decomposition are anomalous, though there are parallels in similar cases, e.g., 2-ethylcyclopentanone¹⁹ and norcamphor.³ One possibility is that the highly excited triplet cyclopentanone molecule produced by mercury photosensitisation crosses over to the excited singlet ketone before decomposition. It is difficult to believe that this process is so efficient that no aldehyde is formed. An alternative explanation which appears to be more satisfactory is that the higher vibrational levels of the triplet dimethylcyclopentanone can give rise to hydrocarbon products. Indeed it is possible to construct a mechanism to explain our experimental findings where all the products result from only the triplet state. An abbreviated form of this mechanism is shown in Scheme 4. The sub-

trans-2,3-DMCP +
$$h\nu \longrightarrow S_a$$
 I_a
 $S_a + M \longrightarrow S_0 + M$ k_4
 $S_a \longrightarrow T_a'$ k_{10}
 $S_0 \longrightarrow T_a''$ k_9
 $T_a' \longrightarrow$ hydrocarbons + CO k_{11}
 $T_a'' \longrightarrow$ aldehydes + ketones k_{12}
SCHEME 4

scripts refer to vibrational excitation. For simplicity only four levels are considered though in fact a whole spectrum could occur. It is suggested that hydrocarbon products arise from the higher vibrational levels of the triplet dimethylcyclopentanone whereas the aldehyde products arise from the lower and lowest levels. The mercury-photosensitisation results then arise naturally. Similarly the results obtained with short-wavelength radiation and also the benzene photosensitisation are reasonable. The quantitative interpretation of the latter is probably complicated by the presence of both excited singlet and triplet state benzene capable of transferring different amounts of energy.

At first sight an objection to this mechanism seems to be presented by the quenching results in the gas phase. The relatively small effects of oxygen and penta-1,3-diene do not seem to be consistent with their known high

¹⁹ R. Srinivasan and K. A. Hill, J. Amer. Chem. Soc., 1965, 87, 4988.

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efficiency in quenching triplets. We suggest that this apparent anomaly arises because of the very rapid rate of decomposition of the vibrationally excited triplet dimethylcyclopentanone molecules. Thus while the excited singlet molecules survive sufficiently long to lose vibrational energy collisionally even at quite low pressures, and hence to affect the energy content of the triplets and thus ultimately the relative product yields, this is not true at reasonable pressure of the triplets. This explanation also accounts for the results obtained in solution. Under these conditions there will be time for vibrational deactivation of the triplets leading to molecules with little vibrational excitation, and these may be quenched by piperylene.

A stationary-state treatment of the second mechanism can be carried out and yields results fully consistent with the reported experimental findings. Unfortunately a combination of both mechanisms presented is also capable of encompassing all the results. Thus we cannot rule out the possibility that the hydrocarbons result directly from both singlet and triplet states. On the basis of simplicity alone the second mechanism must be preferred, but more data are needed before the more complex possibility can be ruled out.

Finally we note that both *trans*-2,3-dimethylcyclopentanone and the mixture of *cis*- and *trans*-2,3-dimethylcyclopentanone gave the same ratio of products with only two exceptions. This is further evidence that the decomposition proceeds through a photo-equilibrium configuration.⁴ That two of the ratios differ can be rationalised on the basis of the lower thermodynamic stability of the *cis*-2,3-isomer. Without more precise data further discussion of this point is not profitable.

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