that environment. Thus, the hydrocarbon chains on membrane phospholipids can be thought of as nearly rigid rods ($P_t \sim 0.96$), at least for the regions where $n < 10$.

Results of experiments on membranes labeled with IV(m,n) must be interpreted with caution, since membrane preparations have the enzymatic capacity to de-

grade phospholipids. Our experiments with phospholipases A and D indicate, however, that these enzymes degrade IV(10,3) and IV(7,6) very slowly relative to natural lecithin, while degradation of IV(5,10) is nearly as rapid as that for the natural substrate. Use of IV-(m,n) with $n < 6$ as membrane labels may then overcome the anticipated problem of *in vivo* degradation.

Structure and Reactivity in the Vapor-Phase Photolysis of Ketones. XV. Methyl Cyclopropyl Ketone[1a-c]

Dana G. Marsh[1d] and J. N. Pitts, Jr.*

Contribution from the Department of Chemistry, University of California, Riverside, California 92502. Received April 24, 1970

Abstract: The vapor-phase photochemistry of methyl cyclopropyl ketone has been reinvestigated. Methyl cyclopropyl ketone undergoes a Norrish type I split to yield carbon monoxide and radical fragments at 3130 and 2537–2654 Å. Methyl cyclopropyl ketone also photoisomerizes *via* a π^*-assisted cyclopropane fission to yield methyl *cis*-propenyl ketone, methyl *trans*-propenyl ketone, and methyl allyl ketone in a primary process. The quantum yields for carbon monoxide and the three photoisomers formed in a primary process in the photolyses of methyl cyclopropyl ketone vary with temperature, pressure, and wavelength, but are independent of light intensity. The results of quenching experiments at 2537–2654 Å with TME (2,3-dimethyl-2-butene), molecular oxygen, and nitric oxide and with piperylene at 3130 Å indicate that the reactions are occurring from the first excited *singlet* state of methyl cyclopropyl ketone. Furthermore, the pressure, temperature, and wavelength dependence of the quantum yields suggests that the products arise from vibrationally excited levels of this first excited singlet state.

The vapor-phase photochemistry of methyl cyclopropyl ketone was first reported by Pitts and Norman in 1954,[1a] who identified the major primary product as methyl propenyl ketone. It was reported that methyl *cis*-propenyl and methyl *trans*-propenyl ketones were formed, but their relative amounts were not determined. They reported in detail upon the formation of secondary radical products.

The efficiency of the temperature-independent (25–120°) rearrangement ($\Phi = 0.3$) of methyl cyclopropyl ketone to methyl propenyl ketone compared to free radical and carbon monoxide production ($\Phi = 0.1$) suggested the use of the cyclopropyl group as a "structural probe" in aliphatic ketone series to investigate energy transfer from the excited carbonyl group (n,π^*) to the cyclopropyl ring.[1b,c]

This paper presents detailed studies on the photoisomers formed from methyl cyclopropyl ketone in *primary* processes and the nature of the excited state involved. A mechanistic interpretation of the results is given.

Experimental Section

Apparatus and Procedure. The photochemical apparatus consists of a medium-pressure mercury-arc ultraviolet light source, a system of filters to isolate narrow-wavelength regions of the ultraviolet spectrum, an optical quartz reaction chamber and pumping system, two RCA 935 photodiodes utilized in a Wheatstone bridge circuit for measurements of relative radiant energy, a Toepler

pump and gas buret system for quantum yield and actinometric determinations, and a conventional high-vacuum system for handling gases and liquids.

A Hanovia Type A medium-pressure mercury arc was used for all analytical studies. The lamp was mounted in a water- and air-cooled housing. The lamp was operated at 500 W (150 V and 3.3 A) by an inductance-stabilized 165-V output transformer, with input voltage provided by a Sola 1000-W ac voltage stabilizer. When used in this arrangement the lamp was quite stable, the light intensity varying less than 3% over a period of months.

Two wavelength regions were used during the study. A Jena Glaswerk 3130-Å interference filter system was used for longer wavelength studies, whereas a 4.5-cm-path chlorine vapor filter (at 1 atm) in series with a 2-mm-path Corning 7-54 (red-purple Corex) were used for the 2537–2654-Å region.

Quartz lens systems were used to collimate and focus the light such that a parallel beam of light completely illuminated the quartz reactor vessel and impinged upon the RCA 935 photodiode. A portion of the incident light is reflected off a quartz plate set at about 45° into another RCA 935 photodiode. These photodiodes are employed in two arms of a Wheatstone bridge circuit. When a high-sensitivity galvanometer is used as a nulling device, this arrangement allows the measurement of small fractions of absorbed light (corresponding to low-pressure runs) with an uncertainty less than 2%.

The quartz reactor vessel (2.5 × 20 cm) was contained within a cylindrical aluminum furnace, the temperature of which could be varied between room temperature and 350° and automatically controlled to within 2% at any temperature. The reactor vessel was contained in a closed loop with an all-glass pumping device which continuously circulates starting material and reaction products. This pumping and short photolysis times (low chemical conversions) serve to minimize or eliminate unwanted secondary reactions.

Quantum yield measurements for the formation of carbon monoxide and methane and actinometric determinations were made using a combination Toepler pump–gas buret assembly. The top of the gas buret was modified such that samples could be withdrawn in sample stopcocks and mass spectral or gas chromatographic determinations could be made. Starting ketone and prod-

(1) (a) Paper I, J. N. Pitts, Jr., and I. Norman, *J. Amer. Chem. Soc.*, **76**, 4815 (1954); (b) paper IV, L. D. Hess and J. N. Pitts, Jr., *ibid.*, **89**, 1973 (1967); (c) paper V, L. D. Hess, J. L. Jacobson, K. Schaffner, and J. N. Pitts, Jr., *ibid.*, **89**, 3684 (1967); (d) taken from the doctoral dissertation of D. G. Marsh, University of California, 1969.

Table I. Data Table for Methyl Cyclopropyl Ketone Photolyses at 3130 Å and 120° [a]

No.	Pressure, mm	Time, sec × 10³	$I_0 \times 10^9$ einsteins/sec	Q_m	NO, mm	Piperylene, mm	Cis	Trans	Allyl
							Quantum yields		
40	48	4.8	2.13	0.286			0.088	0.014	0.011
42	41	22.3	2.13	0.188			0.090		
43	57	7.2	2.13	0.340			0.090	0.017	0.010
44	102	7.4	2.13	0.460			0.100	0.018	0.011
53	11.7	9.75	3.18	0.048		4.8	0.080	0.012	
54	15.0	13.5	3.18	0.065			0.086	0.025	
57	20.5	14.6	3.18	0.096	3.0		0.080		
58	20.5	13.3	3.18	0.091		0.2	0.090		
59	20.2	13.2	3.18	0.096			0.085		
60	24.0	13.6	3.18	0.096		1.0	0.090		

[a] Data from this table are presented in Figure 1.

Table II. Data Table for Methyl Cyclopropyl Ketone Photolyses at 2537–2654 Å [c]

No.	Pressure, mm	Temp, °C	Time, sec	$I_0 \times 10^9$ [a]	Q_m	Cis	Trans	Allyl	CO	CH₄
						Quantum yield				
69	43	120	3,600	5.64	0.734	0.211	0.109	0.076	0.077	0.016
70	44	120	900	5.64	0.734	0.229	0.105	0.094		
71	44	120	1,530	5.64	0.742	0.239	0.110	0.090		
72	46	120	14,400	5.64	0.734	0.150	0.090	0.056	0.057	0.016
73[b]	48	120	2,000	5.64	0.734	0.210	0.110	0.080		
74	21.5	170	1,800	5.64	0.462	0.234	0.200	0.077	0.170	0.050
91	18.2	60	900	5.64	0.482	0.250	0.156	0.060		0.040
92	18.2	60	900	5.64	0.482	0.250	0.156	0.060		
93	18.2	227	900	5.40	0.400	0.210	0.200	0.042		
95	22.8	227	900	5.40	0.457	0.240	0.200	0.040	0.210	0.110
96	25.0	283	900	5.40	0.457	0.220	0.214	0.040	0.220	0.200
97	22.0	183	900	5.40	0.462	0.238	0.191	0.042	0.190	0.060
75	20.8	120	3,200	5.64	0.465	0.224	0.155	0.082	0.106	0.011
76	3.0	120	2,000	5.64	0.165	0.200	0.200	0.050	0.200	
77	69.0	120	3,400	5.64	0.892	0.190	0.083	0.067	0.045	0.012
78	1.8	120	4,400	5.64	0.112	0.185	0.207	0.036		
102	20.0	120	900	5.60	0.455				0.150	0.020

[a] Incident intensity, I_0, in units of einsteins sec⁻¹. [b] Run 73 has 10.2 mm of nitric oxide as an added gas. [c] Data from this table are presented in part in Figures 2 and 3.

ucts condensable at liquid nitrogen temperature (−197°) were removed and aliquots analyzed by glpc. An Aerograph Model 202-2B dual column thermocouple detector instrument was used with a 20 ft × 0.25 in., 20% TCEP (1,2,3-tris(2-cyanoethoxy)-propane) on 60–80 Chromosorb P (A/W HMDS) column. This column is efficient for separating the photoisomers formed in the photolysis of methyl cyclopropyl ketone. Compounds collected from the chromatograph were subjected to mass spectral, ultraviolet, infrared, and nmr analyses. For quantitative measurements, the detector was calibrated in terms of peak area units per micromole of compound.

Materials. Diethyl ketone, having a quantum yield of carbon monoxide Φ = 0.97,[1b] was used for actinometric measurements. Dark runs were performed at all temperatures reported and methyl cyclopropyl ketone is thermally stable under all conditions. Chemical conversions were restricted to a few per cent for all runs.

Methyl cyclopropyl ketone is available commercially. This ketone was subsequently repurified by spinning band distillation (Nester/Faust Annular Teflon). The fraction used for photolyses was 99.95% pure as determined by glpc. Methyl trans-propenyl ketone and methyl allyl ketone are available commercially. Methyl cis-propenyl ketone was obtained by photoisomerization of the trans isomer. Diethyl ketone was obtained commercially and repurified by spinning band distillation. A 99.9% pure fraction was used for all actinometry.

Results

The vapor-phase photolysis of methyl cyclopropyl ketone with 3130- and 2537–2654-Å light results in the formation of four major products. Carbon monoxide results from a Norrish type I elimination, and photochemical rearrangement of the cyclopropyl ring leads to the formation of three photoisomers, methyl cis-propenyl ketone, methyl trans-propenyl ketone, and methyl

allyl ketone. These four major photoproducts are formed in primary steps. Additionally, many other products were formed in minor amounts via secondary radical reactions. Identified were methane, ethane, cyclopropane, ethylene, propylene, and biallyl. Of the minor products formed in secondary reactions, only methane was monitored.

Results of Photolyses at 3130 Å. The quantum yields for formation of the three photoisomers and carbon monoxide at 120° are Φ_{cis} = 0.09, Φ_{trans} = 0.017, Φ_{allyl} = 0.011, and Φ_{CO} = 0.04. These quantum yields are independent of light intensity, irradiation time, and pressure of starting ketone. Data are shown in Table I.

Quenching experiments with piperylene were performed. Figure 1 shows the effect of quencher upon the quantum yield for formation of methyl cis-propenyl ketone. The quantum yield (Φ = 0.09) is independent of the pressure of added piperylene.

Results of Photolyses Using 2537–2654-Å Light. The results reported here are for the direct photochemical excitation of methyl cyclopropyl ketone. Data are presented in Tables II and III. Mercury sensitization is not important in this system for two reasons. First, a medium-pressure "self-reversed" lamp was used.[2] Second, several experiments were performed in which a mercury filter was interposed between the lamp and the

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

Table III. Data Table for Methyl Cyclopropyl Ketone Photolyses at 2537-2654 Å in the Presence of Added Gases at 120° [d]

| No. | Pressure, mm | Time, sec | $I_0 \times 10^9$ [a] | Q_m | Added gas, mm | | | | Quantum yields | | | | |
					O_2	NO	CO_2	Quencher [b]	Cis	Trans	Allyl	CO	CH_4
25	26.5	7,400	5.10	0.605			102		0.203	0.093	0.059		
26	29.0	3,600	5.10	0.595			266		0.207	0.067	0.052	0.076	0.005
89	19.5	900	5.53	0.458	330				0.230	0.097	0.052		
90	20.0	900	5.53	0.457		248			0.110	0.070	0.023		
98	20.0	8,800	0.61	0.460					0.242	0.176	0.046	0.140	0.040
99	20.0	68,300	0.07	0.460					0.221	0.178	0.035	0.140	0.080
100 [c]	20.0	800	5.60	0.455					0.200			0.100	0.020
101 [c]	21.0	800	5.60	0.455					0.200	0.160	0.034	0.090	0.013
61	9.2	7,200	5.64	0.317					0.218	0.184			
62	8.6	7,700	5.64	0.295					0.210	0.165			
63	8.2	7,200	5.64	0.288				1.0	0.210	0.169			
64	8.7	6,030	5.64	0.297				4.8	0.230	0.170			
66	8.4	3,700	5.64	0.290					0.216	0.177	0.067	0.180	0.013
67	8.3	1,800	5.64	0.280					0.220	0.183	0.080	0.176	0.013
68	8.9	900	5.64	0.290					0.214	0.176	0.072		
79	21.0	900	5.64	0.470				5.0	0.231	0.140	0.067	0.130	0.040
81	20.0	1,050	5.64	0.467					0.220	0.150	0.055		
82	20.2	900	5.64	0.467					0.247	0.165	0.054	0.140	0.050
83	20.0	1,050	5.53	0.470				16.0	0.206	0.128	0.043		
84	19.8	1,200	5.53	0.474				28.7	0.208	0.100	0.043	0.071	0.056
85	7.7	920	5.53	0.300					0.230	0.196	0.041		
86	7.7	905	5.53	0.300				4.6	0.230	0.185	0.044		
87	7.7	900	5.53	0.300				10.0	0.222	0.164	0.046		

[a] Incident light intensity, I_0, in units of einsteins sec^{-1}. [b] 2,3-Dimethyl-2-butene used as quencher at 2537-2654 Å. [c] Mercury filter used for these runs. [d] Data from this table presented in Figures 4-6.

reactor cell. This filter would totally absorb any resonance 2537-Å radiation from the lamp. In all these runs no evidence for mercury sensitization was found in changed product distributions or quantum yields.
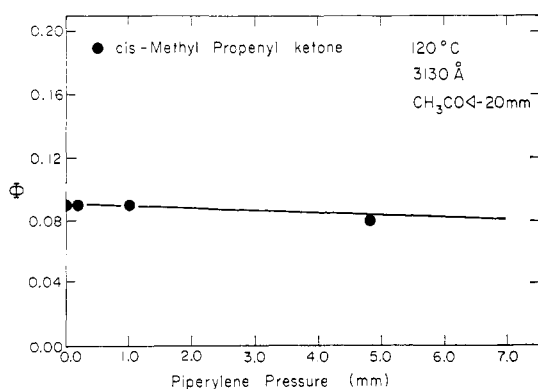

Figure 1. Quantum yield of methyl *cis*-propenyl ketone as a function of added pressures of piperylene at 3130 Å and 120°; constant pressure of methyl cyclopropyl ketone (20 mm).

Quantum yields for formation of the four major photoproducts exhibit pressure dependence, and this is shown in Figure 2. It is apparent from this figure that there are two families of curves. The curves showing quantum yields of formation of methyl *cis*-propenyl ketone and methyl allyl ketone behave similarly, increasing from low-pressure minima, reaching maximum values at about 20–30 mm, and then decreasing at higher pressures. The curves for the quantum yields for formation of carbon monoxide and methyl *trans*-propenyl ketone also behave in a like manner, decreasing continuously with increasing pressure of starting ketone. In general, the quantum yields for the formation of the four major products are greater than those values obtained using 3130-Å light.

The temperature dependence of the quantum yields for formation of the four major photoproducts and methane is shown in Figure 3. In these temperature experiments, the number of moles of methyl cyclopropyl ketone was varied such that the pressure was held at 21 ± 4 mm for the series. This ensures that
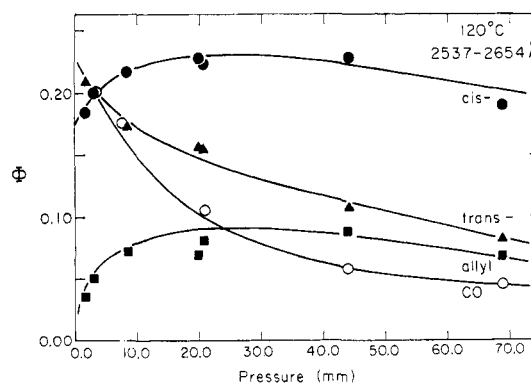

Figure 2. Quantum yields as a function of methyl cyclopropyl ketone pressure at 2537-2654 Å and 120°: ●, methyl *cis*-propenyl ketone; ▲, methyl *trans*-propenyl ketone; ■, methyl allyl ketone; ○, carbon monoxide.

collisional deactivation of vibrational states is approximately the same at each temperature. The quantum yield for formation of methane exhibits strong temperature dependence, increasing sharply above 500°K. The quantum yields for formation of methyl *cis*-propenyl ketone and methyl allyl ketone behave similarly; both decrease slightly with increasing temperature, whereas the quantum yields for formation of carbon monoxide and methyl *trans*-propenyl ketone increase slightly with increasing temperature.

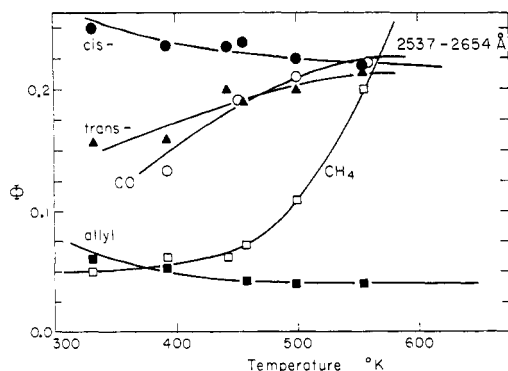The light intensity dependence of quantum yields for formation of the four major products and methane is

Figure 3. Quantum yields as a function of temperature at 2537-2654 Å: ●, methyl cis-propenyl ketone; ▲, methyl trans-propenyl ketone; ■, methyl allyl ketone; ○, carbon monoxide; □, methane.
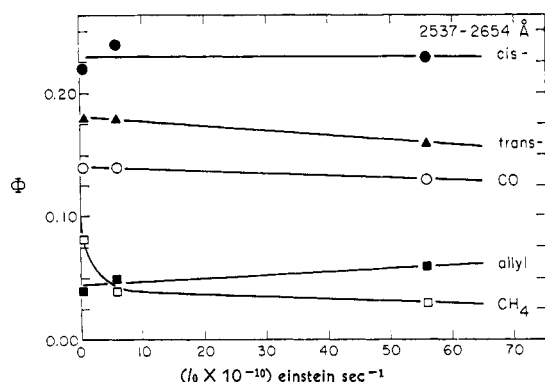

Figure 4. Quantum yields as a function of light intensity at 2537-2654 Å and 120°; constant pressure of methyl cyclopropyl ketone (20 mm); values for light intensity, 0.7×10^{-10}, 6.1×10^{-10}, and 56.4×10^{-10} einstein sec^{-1}: ●, methyl cis-propenyl ketone; ▲, methyl trans-propenyl ketone; ■, methyl allyl ketone; ○, carbon monoxide; □, methane.
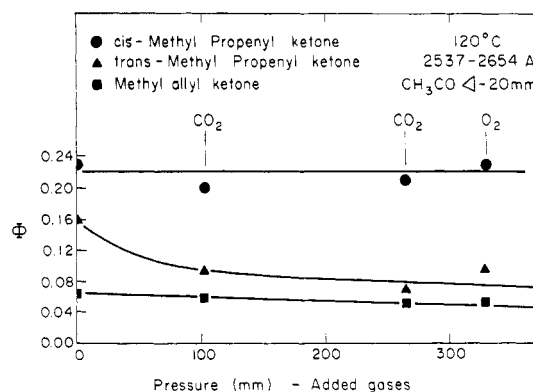

Figure 5. Quantum yields as a function of the pressures of added gases; constant pressure of methyl cyclopropyl ketone (20 mm); 102 and 266 mm of carbon dioxide added and 330 mm of oxygen added: ●, methyl cis-propenyl ketone; ▲, methyl trans-propenyl ketone; ■, methyl allyl ketone.

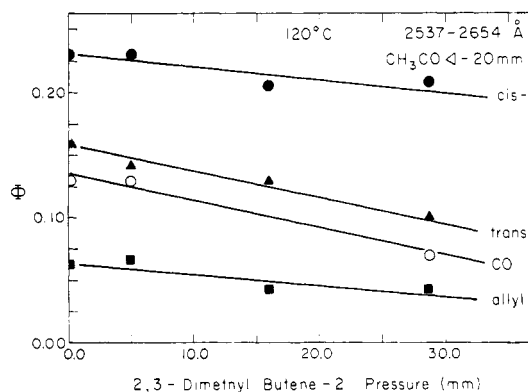

Figure 6. Quantum yields as a function of added pressure of 2,3-dimethyl-2-butene; constant pressure of methyl cyclopropyl ketone (20 mm): ●, methyl cis-propenyl ketone; ▲, methyl trans-propenyl ketone; ■, methyl allyl ketone; ○, carbon monoxide.

shown in Figure 4. The quantum yield for formation of methane is different from that of the others in that it increases sharply at low light intensities. The quantum yield for formation of methyl cis-propenyl ketone remains constant; that of methyl allyl ketone increases very slightly, whereas those for formation of carbon monoxide and methyl trans-propenyl ketone decrease slightly. The light intensity was varied from 0.7×10^{-10} to 56.4×10^{-10} einstein sec^{-1}.

Figure 5 shows the effect of added gases on the quantum yields for formation of the photoisomers. The pressure of added carbon dioxide was either 100 or 260 mm, and that of oxygen was 330 mm. The pressure of methyl cyclopropyl ketone was held constant at 20 mm. The points at zero pressure are average values for the quantum yield for formation of the three isomers at 20 mm methyl cyclopropyl ketone pressure in the absence of foreign gases. The curves for the formation of methyl cis-propenyl ketone and methyl allyl ketone behave similarly and their quantum yields are constant, that is, independent of added pressures of carbon dioxide and oxygen. The quantum yield for formation of methyl trans-propenyl ketone decreases with increasing pressure of added gases.

The effect of a triplet-state quencher upon the quantum yields for formation of the four major products is shown in Figure 6. Tetramethylethylene (2,3-dimethyl-2-butene) was added to 20 mm of methyl cyclo-

propyl ketone. Once again, a similarity is apparent in the behavior of the quantum yields for formation of carbon monoxide and methyl trans-propenyl ketone, vs. methyl cis-propenyl ketone and methyl allyl ketone. The quantum yields for formation of methyl cis-propenyl ketone and methyl allyl ketone decrease slightly with increasing pressure of tetramethylethylene. The quantum yields for formation of carbon monoxide and methyl trans-propenyl ketone decrease more strongly.

Discussion

Discussion of 3130-Å Photolyses. Methyl cyclopropyl ketone has an ultraviolet absorption spectrum typical of any nonconjugated ketone. The n,π* band extends from about 2250 Å through a maximum at 2750 Å and terminates at 3150 Å. The photolyses performed with 3130-Å light are thus just sufficiently energetic to excite methyl cyclopropyl ketone in its n-π* transition.

The quenching experiments with piperylene indicate a *singlet* state is responsible for the photochemistry observed. Figure 1 shows that the quantum yield for formation of methyl cis-propenyl ketone is independent of added pressures of piperylene. The other two photoisomers and carbon monoxide also have quantum yields for formation that are unaffected by added pressures of piperylene. If a triplet state were involved be-

sides the singlet state, the quantum yields for products arising from the triplet state would decrease corresponding to quenching of that electronically excited state, then level off, and finally begin to decrease very slowly again due to collisional deactivation of the vibrational excited levels in the first excited singlet state.[3] At 3103 Å the quantum yields remain constant with increasing pressures of piperylene, which indicates that neither electronic quenching of a triplet state nor collisional deactivation of a singlet state is occurring.

Discussion of 2537–2654-Å Photolyses. These photolyses correspond to excitation in the n,π^* band near the absorption maximum, and the four major products are formed with greater quantum efficiencies than they were in photolyses using 3130-Å light.

The pressure dependences of the photoproducts are interpreted in the following way. The carbon monoxide and methyl *trans*-propenyl ketone arise from a high vibrational level(s) in the first excited singlet state. The methyl *cis*-propenyl ketone and methyl allyl ketone are formed from a lower lying vibrational level(s) in the first excited singlet state. (Quenching experiments at 2537–2654 Å will be discussed later; however, the results will be seen to be entirely analogous to those obtained in the 3130-Å region with piperylene.) As the quantum yields for the formation of carbon monoxide and methyl *trans*-propenyl ketone decrease, there are approximately compensating increases in the quantum yields for the formation of methyl *cis*-propenyl ketone and methyl allyl ketone. As the total pressure of the system increases, the vibrational level(s) responsible for the production of the trans-isomer and carbon monoxide is deactivated by collisions while the vibrational level(s) responsible for the methyl allyl ketone and methyl *cis*-propenyl ketone are populated by collisions faster than they are depopulated up to about 30 mm. At pressures greater than 30 mm all vibrational levels responsible for product formation are deactivated by collisions. The sum of the quantum yields for the four major products is nearly constant (Φ = 0.6) up to 20 mm which supports this interpretation.

The strong dependence of the quantum yield for methane upon increasing temperature as shown in Figure 3 is analogous to that observed for methane formed in free-radical mechanisms in similar systems.[4,5] The dependences of the quantum yields for formation of the four major photoproducts upon temperature and light intensity suggest thay are not formed in secondary processes *via* free-radical mechanisms. Although they show some temperature dependence, it is not at all like the temperature dependence for methane. The quantum yields for formation of methyl *trans*-propenyl ketone and carbon monoxide again exhibit similar behavior, as do the quantum yields for formation of methyl *cis*-propenyl ketone and methyl allyl ketone. The temperature dependence of these four photoproducts may be interpreted as follows. At any temperature, a Boltzmann distribution of vibrational levels in the ground electronic state of methyl cyclopropyl ketone will result. A high temperature will favor the population of higher vibrational levels in the ground

state. If photoexcitation to the first excited singlet state is done with light of a fixed wavelength but at different temperatures, the different distributions of molecules among the vibrational levels in the excited state corresponding to different temperatures may be attributed to differences in the Boltzmann distributions of vibrational levels in the ground electronic states. This fact has been used previously to explain the temperature dependence for the primary quantum yield in ketene photolyses.[6–8] It cannot be claimed, *a priori*, that a conservation of vibrational temperature will occur upon excitation from the ground electronic state to an excited state, because of differences in vibrational spacings, selection rules, and Franck–Condon factors. However, quite apart from the conservation of vibrational temperature, for light of a fixed wavelength, a molecule occupying a high vibrational level in the ground state will attain a high vibrational level in the excited state. Thus, increasing the temperature favors the population of higher vibrational levels in the excited state. The results from the pressure study suggest that carbon monoxide and methyl *trans*-propenyl ketone arise from higher vibrational levels in the first excited singlet state than do methyl *cis*-propenyl ketone and methyl allyl ketone. The temperature results are entirely consistent with this conclusion. The higher temperature photolyses enhance the formation of the carbon monoxide and methyl *trans*-propenyl ketone, as shown by their increasing quantum yields. On the other hand, the quantum yields of methyl *cis*-propenyl ketone and methyl allyl ketone decrease relative to their values at lower temperatures.

This argument seems good qualitatively but is not necessarily valid quantitatively. An alternate explanation may be that there is an activation energy, corresponding to rotation about a carbon–carbon bond perhaps, for the formation of the trans isomer but not for the cis isomer, where no rotation is necessary. The higher temperatures would aid in overcoming this barrier, and the yield of trans isomer would increase at the expense of the yield of cis isomer. An Arrhenius plot of $\log ((1/\Phi) - 1)$ *vs.* T^{-1} was rather scattered and did not provide a linear relationship from which an activation energy could be calculated.

It is interesting that at temperatures greater than 170°, the sum of the quantum yields for the four major photoproducts is constant (Φ = 0.7). This suggests a relationship between the upper level(s) responsible for formation of trans isomer and carbon monoxide, and the lower level(s) from which cis and allyl isomers are produced. In this respect, the temperature dependence is quite analogous to the pressure dependence observed.

The variations of quantum yields with light intensity are shown in Figure 4. Once again methane is included to show the effect of light intensity on a product formed in a free-radical secondary mechanism. The sharp rise in quantum yield for formation of methane at low light intensities is typical for a free-radical mechanism, and by comparison it is evident that the other photoproducts are not formed in secondary free-radical mechanisms.[4] The fact that the quantum yields for

(3) J. W. Coomber and J. N. Pitts, Jr., *J. Amer. Chem. Soc.*, **91**, 547 (1969).

(4) D. G. Marsh, E. Heine, and J. N. Pitts, Jr., *Trans. Faraday Soc.*, **64**, 549 (1968).

(5) G. Greig and J. C. J. Thynne, *ibid.*, **63**, 1369 (1967).

(6) B. T. Connelly and G. B. Porter, *Can. J. Chem.*, **36**, 1640 (1958).

(7) A. N. Strachan and W. A. Noyes, Jr., *J. Amer. Chem. Soc.*, **76**, 3258 (1954).

(8) G. B. Porter and B. T. Connelly, *J. Chem. Phys.*, **33**, 81 (1960).
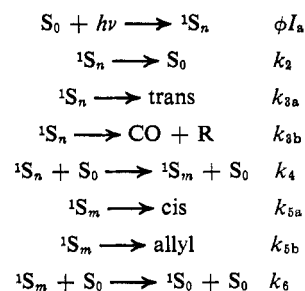
formation of major photoproducts are independent of light intensity is important, since this means that the differences in quantum yields at the two wavelength regions are real, that is, not an artifact caused by differences in absorbed light intensity. If the ratios of the quantum yields for the formation of methyl *cis*-propenyl ketone and methyl *trans*-propenyl ketone at the two wavelengths are compared, further evidence is obtained for the idea that carbon monoxide and methyl *trans*-propenyl ketone occur from higher vibrational levels in the first excited singlet state and methyl *cis*-propenyl ketone and methyl allyl ketone from lower levels. The ratio of the cis isomers is $\Phi_{2537-2654}/\Phi_{3130} = 2.5$ and of the trans isomers is $\Phi_{2537-2654}/\Phi_{3130} = 8.0$. We have already said that the photolyses using 3130-Å light are just sufficiently energetic to populate the vibrational manifold in the first excited singlet state. On the other hand, using 2537–2654-Å light, there is adequate energy to populate highly excited vibrational levels in the excited singlet state. One would expect to see a larger change in quantum yield upon changing from the 3130- to the 2537–2654-Å region for products arising from higher vibrational levels, since the low vibrational levels should be populated well at either wavelength. The wavelength data suggest that the methyl *trans*-propenyl ketone occurs from a higher vibrational level(s) than the methyl *cis*-propenyl ketone, and this is consistent with the pressure and temperature results.

Quenching experiments using 2537–2654-Å light were carried out by adding pressure of tetramethylethylene (2,3-dimethyl-2-butene, TME). Figure 6 shows that the quantum yields for all products decrease slightly upon addition of up to 30 mm of quencher to 20 mm of methyl cyclopropyl ketone. As before, two families of curves are apparent, methyl *cis*-propenyl ketone and methyl allyl ketone belonging to one family and methyl *trans*-propenyl ketone and carbon monoxide to the other. The decreases in quantum yields are not consistent with the quenching of an electronically excited triplet state; they are, however, consistent with collisional deactivation of the vibration levels in the first excited singlet state by a molecule (TME) having a large number of degrees of vibrational freedom. The fact that the compounds carbon monoxide and methyl *trans*-propenyl ketone are deactivated more strongly with increasing pressure is consistent with the proposal that these compounds are occurring from a higher vibrational level(s).

In Figure 5 are the results of adding an inert gas, carbon dioxide, and molecular oxygen, a known triplet-state quencher and radical scavanger. Carbon dioxide is added to the reaction to test whether heterogeneous reactions (wall reactions) are important. The quantum yields for the family of products represented by methyl *cis*-propenyl ketone and methyl allyl ketone are unaffected by additions of carbon dioxide, whereas the quantum yield for methyl *trans*-propenyl ketone decreases slightly with increasing pressure. This is consistent with the notion that the trans isomer is occurring from a higher vibrational level(s), and, compared with collisional deactivation by TME, a much greater pressure of added carbon dioxide is required to decrease the quantum yield because carbon dioxide has only a few degrees of vibrational freedom. The addition of

oxygen at 330 mm causes a decrease in the quantum yield of the trans isomer, but no greater a decrease than is caused by the addition of an equivalent pressure of carbon dioxide. This is further evidence that a triplet state is not involved. The addition of small amounts of nitric oxide, another paramagnetic molecule known to quench triplet states and scavenge radicals, has little effect upon the quantum yields for formation of the four major photoproducts.

The results of these experiments may be described by the following mechanism

$$
\begin{array}{ll}
S_0 + h\nu \longrightarrow {}^1S_n & \phi I_a \\
{}^1S_n \longrightarrow S_0 & k_2 \\
{}^1S_n \longrightarrow trans & k_{3a} \\
{}^1S_n \longrightarrow CO + R & k_{3b} \\
{}^1S_n + S_0 \longrightarrow {}^1S_m + S_0 & k_4 \\
{}^1S_m \longrightarrow cis & k_{5a} \\
{}^1S_m \longrightarrow allyl & k_{5b} \\
{}^1S_m + S_0 \longrightarrow {}^1S_0 + S_0 & k_6
\end{array}
$$

S_0 is the ground electronic state of methyl cyclopropyl ketone. ${}^1S_n$ is the nth vibrational level of the first excited singlet state. ${}^1S_m$ is a lower vibrational level of the first excited singlet state. All vibrational levels below ${}^1S_m$ are deactivated by collision only and do not lead to photoproducts. ${}^1S_0$ is the ground vibrational level or a Boltzmann distribution of levels in thermal equilibrium with the surrounding gas. On the basis of quenching experiments, no triplet states are included in the mechanism. Furthermore, fluorescence from the ${}^1S_0$ state is not included in the mechanism on the basis of experimental results. Cis, trans, and allyl refer to the photoisomers formed.

The following expressions may be derived using steady-state approximations

$$1/\Phi_{\text{trans}} = (k_2 + k_{3a} + k_{3b})/k_{3a} + k_4[S_0]/k_{3a} \quad \text{(I)}$$

$$1/\Phi_{\text{CO}} = (k_2 + k_{3a} + k_{3b})/k_{3b} + k_4[S_0]/k_{3b} \quad \text{(II)}$$

$$1/(\Phi_{\text{CO}} + \Phi_{\text{trans}}) = 1 + k_2/k_3 + k_4[S_0]/k_3 \quad \text{(III)}$$

where $k_3 = k_{3a} + k_{3b}$

$$\Phi_{\text{cis}} + \Phi_{\text{allyl}} =$$

$$k_4 k_5[S_0]/(k_5 + k_6[S_0])(k_2 + k_3 + k_4[S_0]) \quad \text{(IV)}$$

$$\frac{\Phi_{\text{trans}} + \Phi_{\text{CO}}}{\Phi_{\text{cis}} + \Phi_{\text{allyl}}} = k_3/k_4[S_0] + (k_3/k_5)(k_6/k_4) \quad \text{(V)}$$

Expressions I and II are plotted in Figure 7. The reciprocal quantum yields when plotted against pressure yield straight lines. Expression III is plotted in Figure 8. $1/(\Phi_{\text{trans}} + \Phi_{\text{CO}})$ *vs.* pressure yields a straight line with an intercept of 2. Expression IV may be evaluated in two pressure limits. At low pressure, the expression $\Phi_{\text{cis}} + \Phi_{\text{allyl}}$ is predicted to increase with increasing pressure, and at high pressures the expression is predicted to decrease with increasing pressure. At intermediate pressures (20–30 mm by calculation) the expression is expected to reach a maximum. An examination of Figure 2 shows that the curves representing the quantum yields for the cis and allyl photoisomers exhibit the behavior predicted by expression IV.
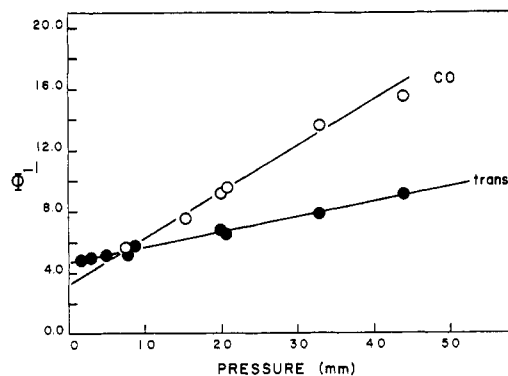
Figure 7. A kinetic plot of Φ^{-1} vs. pressure: $\blacktriangle$, methyl *trans*-propenyl ketone; $\bigcirc$, carbon monoxide.
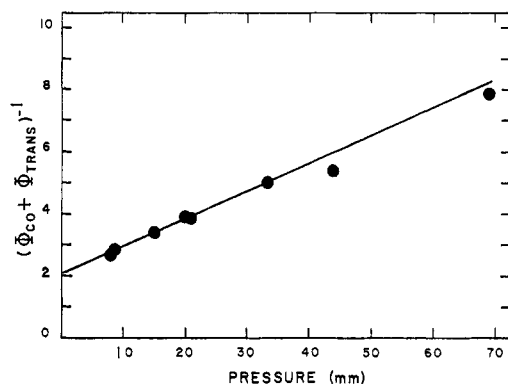

Figure 9. A plot of kinetic expression V.

Figure 8. A kinetic plot of $(\Phi_{CO} + \Phi_{trans})^{-1}$ vs. pressure.

METHYL CYCLOPROPYL KETONE PHOTOPRODUCTS

Figure 10. Norrish type I processes and π^*-assisted cyclopropane fission reactions in methyl cyclopropyl ketone photolyses.

Expression V is plotted in Figure 9 and a straight line is obtained having a slope of k_3/k_4 and intercept of $(k_3/k_5)(k_6/k_4)$. The mechanism predicts that the slopes of the curves in Figures 8 and 9 should be reciprocals. The slopes are 0.09 and 7.5, respectively. Whereas these slopes do not satisfy a reciprocal relationship exactly, the slopes are reciprocal within experimental error because of the large experimental error associated with expression V. The slopes of the lines in Figure 7 yield that $k_{3b} = 3k_{3a}$; the specific rate constant for the formation of carbon monoxide is about three times the rate constant for the formation of the trans isomer. The intercept in Figure 8 yields that $k_2 = k_3$. The rate constant for radiationless return to the ground state is approximately equal to the rate constant $(k_{3a} + k_{3b})$ for the isomerization of the cyclopropyl ring and the formation of carbon monoxide *via* a Norrish type I elimination. Using the data for the slope and intercept in Figure 8 yields a relationship between k_2 and k_4 and shows that k_2 is greater than k_4 by approximately a factor of 10. Recognizing that this is a comparison of a first-order and a second-order rate constant, we see that at least at low pressures, $k_3 = k_2$ is greater than k_4 and product formation can compete with collisional deactivation. The intercept of the curve in Figure 9 is $(k_3/k_5)(k_6/k_4)$. The unimolecular rate constants k_3 and k_5 correspond to similar processes and may be expected to be of the same order of magnitude. As an approximation, with $k_3 = k_5$, the intercept yields $k_6 = 0.4k_4$. The rate constant for collisional deactivation of the ^1S_n vibrational level is greater than the rate constant for the collisional deactivation of the ^1S_m level by a factor
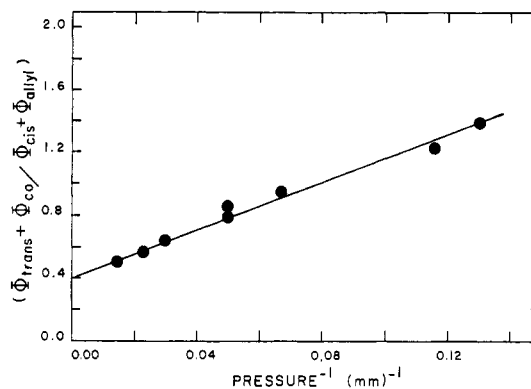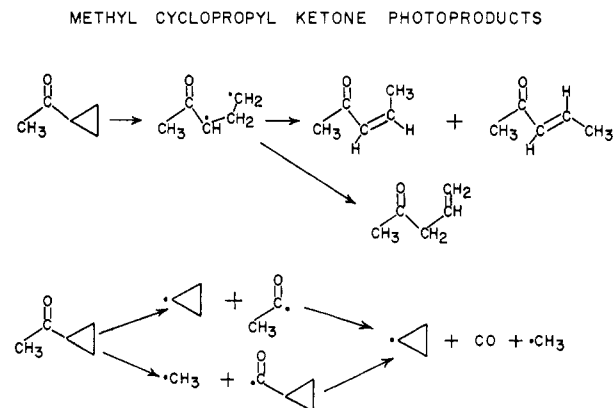
of about 2.5. This agrees with theory.[8] The rate of deactivation by collisions of vibrational levels depends upon the energy of the vibrational level, the higher levels being deactivated with a greater rate constant than the lower levels. The plot of expression V shown in Figure 9 covers the entire pressure region used in the experiments.

The simple mechanism presented predicts the behavior of the photoisomers with pressure, the general shapes of the quantum yield curves, and the complex relationships of the four major photoisomers over the entire pressure region studied. The mechanism used assumes only two vibrational levels, the ^1S_n and ^1S_m, are responsible for product formation. Actually, several closely spaced levels are probably involved since the wavelength is not strictly monochromatic. No mention has been made of the process by which the ^1S_n level(s) is converted to the ^1S_m level(s). Two possibilities exist, the hard collision one-step deactivation, and the many-step cascade collisional deactivation.[8,9] There are insufficient data to warrant a claim for either of the two mechanisms.

The process in which energy is localized in the β bonds of a cyclopropyl ring system after initially being absorbed from a photon in an $\pi^* \leftarrow n$ absorption process leading to bond fission has been termed a π^*-assisted cyclopropane fission (see Figure 10). Pitts and Norman[1] proposed that a biradical intermediate was involved in the process. The current study has no evi-

(9) A. Gandini, D. A. Whytock, and K. O. Kutschke, *Proc. Roy. Soc., Ser. A*, **306**, 541 (1968).

dence either for or against this proposition. However, biradical intermediates have been postulated by other workers on similar systems on the basis of chemical evidence.[10-15]

(10) G. W. Griffin, E. J. O'Connell, and H. A. Hammond, *J. Amer. Chem. Soc.*, **85**, 1001 (1963).
(11) G. W. Griffin, J. Covell, R. C. Peterson, R. M. Dodson, and G. Klose, *ibid.*, **87**, 1410 (1965).
(12) J. K. Crandall, J. P. Arrington, and R. J. Watkins, *Chem. Commun.*, 1052 (1967).
(13) W. G. Dauben and G. W. Schaffer, *Tetrahedron Lett.*, **45**, 4415 (1967).

(14) A. Padwa, E. Alexander, and M. Niemcyzk, *J. Amer. Chem. Soc.*, **91**, 456 (1969).
(15) A. Padwa and D. Eastman, *ibid.*, **91**, 462 (1969).

Photolysis of Cyclopropyl Ketones in the Vapor Phase and in Solution[1,2]

Dana G. Marsh, J. N. Pitts, Jr.,[*3a] Kurt Schaffner,[3b] and Albert Tuinman[3b]

*Contribution from the Department of Chemistry,
University of California, Riverside, California 92502,
and Laboratorium für Organische Chemie der Eidg. Technischen Hochschule, 8006
Zürich, Switzerland. Received April 24, 1970*

Abstract: The vapor-phase (at 120°) and solution photochemistry of dicyclopropyl ketone (I), methyl 2,2-dimethylcyclopropyl ketone (II), cyclopropyl 2,2-dimethylcyclopropyl ketone (III), propyl cyclopropyl ketone (IV), 3-butenyl cyclopropyl ketone (V; in the vapor phase), and 3-methyl-3-butenyl cyclopropyl ketone (VI; in solution) has been investigated. Dicyclopropyl ketone (I), when irradiated in the vapor phase in its n → π* band at 2537–2654 Å, yields cyclopropyl *cis*-propenyl ketone, cyclopropyl *trans*-propenyl ketone, allyl cyclopropyl ketone, and carbon monoxide as major products with quantum yields of 0.125, 0.025, 0.01, and 0.01, respectively. These quantum yields are temperature and pressure independent. Carbon monoxide is formed *via* a Norrish type I elimination, whereas the photoisomers result from a π*-assisted cyclopropane fission reaction. On irradiation of ketone I at 2537 and at 3130 Å in isooctane and benzene solutions, no photochemical reaction is observed. In isopropyl alcohol, however, irradiation leads to reductive cleavage of one ring to yield propyl cyclopropyl ketone (IV). The reaction is presumably due to hydrogen abstraction from the solvent by the excited carbonyl in the primary photochemical process. Ketones II and III, when photolyzed in their n → π* bands at 2537–2654 Å in the vapor phase and at 2537 or 3130 Å in isooctane, benzene, or ethanol solutions, undergo Norrish type II processes to yield 5-methyl-5-hexen-2-one (VII) and 3-methyl-3-butenyl cyclopropyl ketone (VI), respectively. The quantum yields in the vapor phase are 0.30 and 0.25, respectively, and they are independent of pressure. On the basis of experiments with nitric oxide and 2,3-dimethyl-2-butene in the vapor phase, the Norrish type II process for ketones II and III presumably proceeds through their first excited *singlet* state. Infrared spectroscopy evidence for an enol intermediate as the primary photoproduct of II in the vapor phase is presented. Ketones IV and V proved to be quite stable to irradiation in the vapor phase at 2537–2654 Å. Similar photostabilities were observed for ketone IV in isopropyl alcohol and for ketone VI in ethanol solution using 3130-Å light.

In the photolysis of the cyclopropyl ketones I–VI the competition among several intramolecular primary photochemical processes has to be envisaged *a priori:* Norrish type I splits and π*-assisted cyclopropane fissions in all six compounds, Norrish type II processes in ketones II, III, and IV, and oxetane formation (and/or intramolecular energy transfer from the carbonyl group to the double bond) in ketones V and VI. In solution, the intervention of photoreductive processes by intermolecular hydrogen abstraction from appropriate solvent molecules can be expected as well.

This study was undertaken to gain some insight into the competition of such processes in each case. Special emphasis was laid on obtaining evidence regarding the mechanistic differentiation between the cyclopropyl ring fission of ketones I, II, and III in the vapor phase

The vapor-phase photochemistry of dicyclopropyl ketone (I) has been investigated previously by Pitts and Woolfolk[4] and Pitts and Hess.[5] In these two studies, the major products, *cis*- and *trans*-propenyl cyclopropyl ketone, had not been isolated and characterized satisfactorily, the quantum yield determination of product formation required further experimental scrutiny, and the nature of the excited state(s) responsible for the reaction had not been investigated.

(1) Part XVI of the series Structure and Reactivity in the Vapor Phase Photolysis of Ketones [for part XV, see D. G. Marsh and J. N. Pitts, Jr., *J. Amer. Chem. Soc.*, **93**, 326 (1971)], and part LXI of the series Photochemical Reactions [for part LX, see S. Domb, and K. Schaffner, *Helv. Chim. Acta*, **53**, 1765 (1970)].
(2) Taken in part from the doctoral dissertation of D. G. Marsh, University of California, 1969.
(3) (a) University of California, Riverside; (b) Eidg. Technische Hochschule, Zürich.
(4) J. N. Pitts, Jr., and R. W. Woolfolk, Abstracts, 133rd National Meeting of the American Chemical Society, San Francisco, Calif., April 1968, p 4-Q.
(5) J. N. Pitts, Jr., and L. D. Hess, unpublished results.