

The Gas-phase Photolysis of Cyclobutanecarbaldehyde

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The gas-phase photolysis of cyclobutanecarbaldehyde with λ 313 nm at 118° yields CO, cyclobutane, (*E*)-but-2-ene, ethylene, and traces of but-1-ene. CO, cyclobutane, (*E*)-but-2-ene, and but-1-ene are formed *via* initial α -cleavage. It is proposed that ethylene results from a molecular decomposition of vibrationally equilibrated, electronically excited cyclobutanecarbaldehyde. The photolysis is complicated by the thermal trimerization of the aldehyde. The α -cleavage and the fragmentation with formation of ethylene and propenal also occur under conditions of electron impact.

THE gas-phase photolysis of alkanals has been the object of various studies.^{1a} Previously we reported extensively on the gas-phase photolysis of cyclopropanecarbaldehyde.² As an extension, we have now studied the gas-phase photolysis of cyclobutanecarbaldehyde.

RESULTS AND DISCUSSION

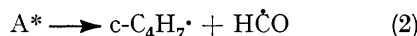
Photolysis.—The gas-phase photolysis of cyclobutanecarbaldehyde with λ 313 nm at 118° yields as gaseous products carbon monoxide, cyclobutane, ethylene, (*E*)-but-2-ene and, for low aldehyde pressures, traces of but-1-ene. None of these products is formed in the absence of irradiation.† The quantum yields of the major gaseous products are given in Table 1. With

TABLE I
Quantum yields in the photolysis of cyclobutanecarbaldehyde with λ 313 nm at 118°

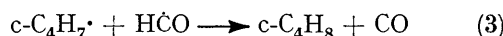
Aldehyde pressure (mmHg)	ϕ			
	CO	Cyclobutane	(<i>E</i>)-But-2-ene	Ethylene
20	1.07	0.66	0.13	0.19
75	1.53	0.84	0.06	0.22

increasing aldehyde pressure, the quantum yields of carbon monoxide and cyclobutane increase, whereas that of (*E*)-but-2-ene decreases. The quantum yield of ethylene seems to be independent of the aldehyde pressure.

The formation of the two major photoproducts may be explained in terms of initial α -cleavage (2) of the



(probably triplet) excited aldehyde,‡ followed by disproportionation (3) of the resulting cyclobutyl and



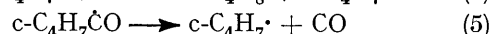
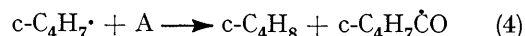
formyl radicals and abstraction of the acyl hydrogen from cyclobutanecarbaldehyde by the cyclobutyl radicals leading to the chain sequence (4) and (5).§ Step (4) is a bimolecular step involving A. Accordingly, the chain

† As monitored by the transmission at 313 nm a thermal conversion of the aldehyde into a more transparent species takes place and eventually an equilibrium is obtained. Its position shifts to the aldehyde side upon heating and to the more transparent species upon lowering the temperature. We suggest that the more transparent species is 2,4,6-tricyclobutyl-1,3,5-trioxan. This compound has, in fact, been obtained as a white solid residue formed after several months in the cyclobutanecarbaldehyde storage tube. The cyclic trimer has been observed before.³

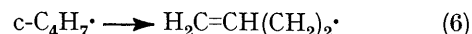
‡ For 313 nm radiation a concerted decarbonylation of (singlet) excited aldehyde is not very likely.

§ Decarbonylation of the analogous acetyl⁴ and propionyl⁵ radicals is very efficient at 118°.

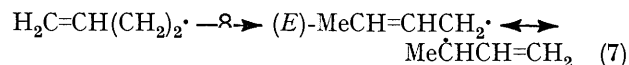
reaction will be of more importance at high aldehyde pressure as is in fact observed (*cf.* $\phi_{\text{cyclobutane}}$, Table 1). The radical chain also explains why ϕ_{CO} exceeds unity.



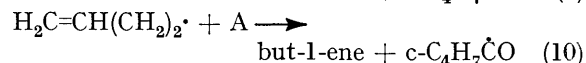
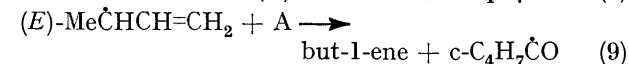
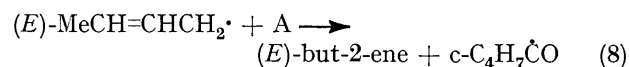
As for the formation of (*E*)-but-2-ene and but-1-ene, ring opening of cyclobutyl radicals is known⁶ to yield but-3-enyl radicals [reaction (6)] which can isomerize



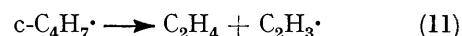
to but-2-enyl radicals [reaction (7)]. Hydrogen abstraction by these radicals then leads to the formation



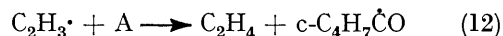
of (*E*)-but-2-ene and but-1-ene [reactions (8)–(10)].



Isomerization (7) only proceeds at elevated temperatures.⁶ Accordingly, it must be assumed that the intermediate but-3-enyl radicals still contain some excess of vibrational energy. The lower $\phi_{(\text{E})\text{-but-2-ene}}$ at high aldehyde pressure is compatible with this assumption in view of the enhanced collisional deactivation of the vibrationally excited but-3-enyl radicals by the aldehyde at the higher pressure. Cleavage of the (vibrationally excited) but-3-enyl radicals yields ethylene and vinyl radicals [reaction (11)]. By hydrogen abstraction the



latter radicals may also end up as ethylene [reaction (12)].



An alternative route to ethylene is the intramolecular reaction (13). This reaction has its thermochemical³

¹ J. G. Calvert and J. N. Pitts, jun., 'Photochemistry,' Wiley, New York, 1966 (a) pp. 368–441; (b) p. 369.

² J. J. I. Overwater and H. Cerfontain, *Rec. Trav. chim. (a)* 1968, **87**, 73; (b) 1970, **89**, 705, 717, 729.

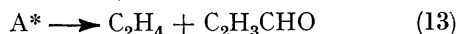
³ B. C. Roquette and W. D. Walters, *J. Amer. Chem. Soc.*, 1962, **84**, 4049.

⁴ J. D. Caldwell and D. E. Hoare, *J. Amer. Chem. Soc.*, 1962, **84**, 3987.

⁵ P. Ausloos, *Canad. J. Chem.*, 1958, **36**, 400; L. C. Fischer and G. L. Mains, *J. Phys. Chem.*, 1964, **68**, 188.

⁶ A. S. Gordon, S. R. Smith, and C. M. Drew, *J. Chem. Phys.*, 1962, **36**, 824.

and electron impact counterparts. An extensive search for the simultaneously produced propenal remained unsuccessful. This is not a strong argument against the occurrence of reaction (13), since propenal can readily

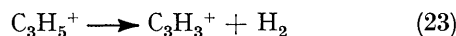
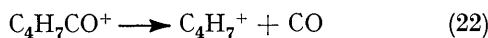
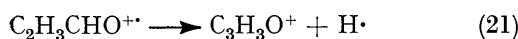
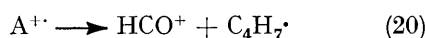
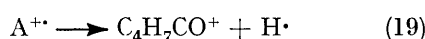
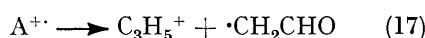
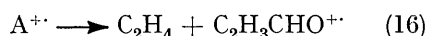
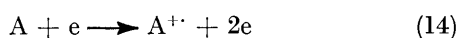


polymerize under the conditions employed. The independence of $\phi_{C_2H_4}$ from the aldehyde pressure renders reaction (11) unlikely in view of the intermediacy of vibrationally excited but-3-enyl radicals. The rate of reaction (11) for thermally equilibrated radicals is negligible.⁶ The independence of $\phi_{C_2H_4}$ from aldehyde pressure indicates that the reacting species in (13) is the vibrational ground state of S_1 or T_1 . Photolysis of phenylcyclobutane yields as major products ethylene and styrene which are formed *via* the vibrational ground state of T_1 .⁷

The gas-phase photolysis of cyclobutyl methyl ketone yields CO, cyclobutane, methane, and ethylene as major products.⁸ The first three products also arise *via* initial α -cleavage, decarbonylation, and subsequent hydrogen abstraction. The ethylene formation, however, was postulated to proceed by reactions (11) and (12).

The gas-phase photolytic behaviour of the present aldehyde differs from that of cyclopropanecarbaldehyde in that the photolysis products mainly arise *via* initial α -cleavage and subsequent radical processes whereas for the cyclopropane analogue the reaction proceeds mainly *via* non-radical isomerization.^{2a,9} The same trend is apparent on comparing the gas-phase photolysis of cyclobutyl methyl ketone⁸ and cyclopropyl methyl ketone.¹⁰

Electron Impact.—The mass spectrum of cyclobutanecarbaldehyde is listed in Table 2. The fragmentation may be explained in terms of the steps (14)–(23).



Steps (15) and (16) are similar to the postulated photochemical route to ethylene. As in the photolysis, α -cleavage [steps (20) and (22)], is important. The α -cleavage of the cyclobutylcarbonyl hydrogen bond [step (19)] has no photochemical counterpart. Cyclo-

⁷ S. Y. Ho, R. A. Gorse, and W. A. Noyes, *J. Chem. Phys.*, **1973**, **77**, 2609.

⁸ I. Norman and J. N. Pitts, jun., *J. Amer. Chem. Soc.*, **1955**, **77**, 6104.

⁹ D. G. Marsh, E. Heine, and J. N. Pitts, jun., *Trans. Faraday Soc.*, **1968**, **64**, 2308.

butanecarbaldehyde under electron impact thus exhibits some fragmentation steps which are similar to those proposed for its gas-phase photolysis.

TABLE 2

The 70 eV mass spectrum of cyclobutanecarbaldehyde

<i>m/e</i>	Relative intensity	Assigned ion composition
84	36	M^+
83	38	$(M - H)^+$
56 (high mass)	14	$C_4H_8^+$
(low mass)	10	$C_3H_4O^+$
55 (high mass)	100	$C_4H_7^+$
(low mass)	36	$C_3H_3O^+$
41	21	$C_3H_5^+$
39	19	$C_3H_3^+$
29 (high mass)	31	$C_2H_5^+$
(low mass)	7	CHO^+
28 (high mass)	29	$C_2H_4^+$
(low mass)	17	CO^+

EXPERIMENTAL

Cyclobutanecarbaldehyde was prepared as described before.¹¹ It was purified by preparative g.l.c. (3.5 m; 25% TCP–firebrick; 95°). After introduction in the high vacuum system it was degassed and distilled twice from 20 to –80°; then it was stored in a black tube at –80°.

The high vacuum apparatus and the optical arrangement to isolate 313 nm radiation have been described in detail.^{2a} The n, π^* molar extinction coefficient of cyclobutanecarbaldehyde in the gas-phase for the isolated 313 nm wavelength was found to be $9.5 \pm 2 \text{ l mol}^{-1} \text{ cm}^{-1}$. The aldehyde conversions in the photolysis were $\leq 5\%$. The gaseous products were analysed as follows. After the irradiation, all products were pumped into the analytical section of the high vacuum system, and those condensable at –200° were trapped. The non-condensable CO and other possible gases present were analysed by means of a copper oxide furnace kept at 280° or by g.s.c. (3 m Porapak Q + 0.5 m molsieves 5A; 25 ml He min⁻¹). A second gas fraction was removed at –105° and analysed by g.l.c. (10 m; 33% dimethylsulpholan–firebrick; 0°; 20 ml He min⁻¹). The products were identified by comparison of their g.l.c. retention times and spectroscopic data with those of authentic samples.

Acetone⁴ and pentan-3-one¹² were used as actinometers.

Mass spectra were obtained with a Varian MAT 711 mass spectrometer.

2,4,6-Tricyclobutyl-1,3,5-trioxan, m.p. 124–125° (lit.,³ 119–120°), had ν_{max} (KBr) 2 980s, 2 880vw, 1 420m, 1 385m, 1 305w, 1 245w, 1 220m, 1 180m, 1 100vs (C–O), 1 005m, 960w, 930w, and 740w cm⁻¹, δ (CDCl₃) 1.7–2.2 (6 H, m, cyclobutylmethylene H), 2.35–2.7 (1 H, m, cyclobutylmethine H), and 4.79 (1 H, d, *J* 6.5 Hz, trioxan H), *m/e* (AET ME902; 70 eV) 251 ($M - H$)⁺, 197, 169, 85, 67, and 55, *m** 42.8 (169 \longrightarrow 85), 52.8 (85 \longrightarrow 67), and 144.9 (197 \longrightarrow 169).

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¹⁰ J. N. Pitts, jun., and I. Norman, *J. Amer. Chem. Soc.*, **1954**, **76**, 4815.

¹¹ C. W. Funke and H. Cerfontain, *J.C.S. Perkin II*, in the press.

¹² L. D. Hess and J. N. Pitts, jun., *J. Amer. Chem. Soc.*, **1967**, **89**, 1973.