The Reactions of Cyclobutadiene

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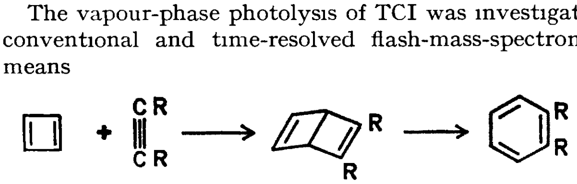
Summary: Cyclobutadiene in the gas phase can be efficiently scavenged with acetylenes to give *ortho*-substituted benzenes and with mono-olefins to give presumably bicyclo[2.2.0]hex-5-enes which undergo cracking and/or photo-induced isomerizations and decomposition.

The u.v. photolysis[1] and oxidative degradation[2] of tricarbonylcyclobutadieneiron (TCI) have been shown to be sources of cyclobutadiene. In the vapour-phase photolysis, the decay of cyclobutadiene produces benzene and acetylene in comparable yields along with smaller quantities of a dimer. We report results related to the photolysis of TCI and to the chemical nature of cyclobutadiene, its reactivity with acetylenes, fluoroethylenes, and oxygen.

The vapour-phase photolysis of TCI was investigated by conventional and time-resolved flash-mass-spectrometric[3] means.



(1)

The results of the earlier experiments[1] were confirmed, on flashing 25 μm TCI vapour with 20 torr He as carrier, benzene and acetylene were formed in about equal yields. The experiment was repeated with 0·50 torr added acetylene, resulting in a sixfold increase in the yield of benzene. On addition of but-2-yne or perfluorobut-2-yne (0·15—0·35 torr), xylene and hexafluoroxylene became the major products with a concomitant suppression of benzene and acetylene. These products can be rationalized in terms of reaction (1). Approximate rate constants measured for the addition reactions are 1×10^7, 0.3×10^7, and 1×10^7 l mole^{-1} sec^{-1} for C_2H_2, C_4H_6, and C_4F_6, respectively, at room temperature.

The intensity variation of the *m/e* 192 parent mass peak of TCI was monitored during the flash. It was observed that the initial rapid decline due to decomposition was followed by a slower growth period during which, in a typical run, about 50% of the initial loss was recovered. This indicates that the primary decomposition step is reversible. Experiments were then conducted with TCI–He–$C^{18}O$ mixtures, in which a considerable fraction of the re-formed TCI was found to contain one, two, or three moles of $C^{18}O$. The following reaction scheme is suggested to account for these observations:

$$\mathrm{TCI} + h\nu \longrightarrow C_4H_4 + Fe(CO)_3$$

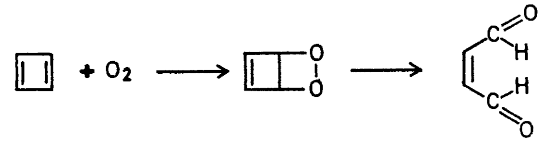
$$Fe(CO)_3 + C^{18}O \longrightarrow Fe(CO)_2C^{18}O + CO, \textit{ etc}$$

$$C_4H_4 + Fe(CO)_2C^{18}O \xrightarrow{M} \mathrm{TCI}$$

Thus, inert gases should suppress cyclobutadiene formation because of their stabilizing effect on reformed TCI This was confirmed by experiments in which the helium carrier was partially replaced with N_2 or CO (5—15 torr) In the course of these experiments it was also observed that the ratio of acetylene to benzene is pressure-dependent and increasing pressure causes the ratio to increase This suggests that in the photolysis of pure TCI, benzene is formed largely through the reaction of cyclobutadiene with its decomposition product acetylene reaction (1) rather than by reaction (2)

$$2\,C_4H_4 \rightarrow C_6H_6 + C_2H_2 \qquad (2)$$

The results obtained in conventional photolyses are shown in the Table TCI neat afforded CO benzene and an iron-containing solid, but not acetylene It appears that under these conditions the acetylene product is removed by secondary photopolymerizations Addition of 20 torr acetylene to the system brought about a sevenfold increase in the benzene yield Addition of large concentrations of but-2-yne or perfluorobut-2-yne resulted in the formation of *o*-xylene and *o*-bistrifluoromethylbenzene in good yields The yields of the two retrievable products, xylenes and CO, were not affected by the presence of a 30-fold excess of an inert gas, CO_2 (800 torr) which fact militates against the involvement of long-lived photoexcited TCI in the mechanism


(3)

Photolysis of TCI with added oxygen gave large amounts of CO_2 and smaller amounts of C_2H_2, C_2H_4 acraldehyde, and furan The primary adduct $C_4H_4O_2$ could not be detected[4] even in flash experiments The nature of the observed products is consistent with the mechanism postulated[5] for the reaction of tetraphenylcyclobutadiene with O_2 [reaction (3)] Malealdehyde is susceptible to polymerization[6] and may decompose photolytically or through interaction with oxygen to give the observed products The large amounts of CO_2 obtained do not necessarily come from the oxidation of cyclobutadiene since photolysis of $Fe(CO)_5$ with added oxygen[7] also produces CO_2

Product yields in the reactions of cyclobutadiene with acetylenes, oxygen, and fluoro olefins

Reactant		TCI	CO	C_6H_6	o Xylene µ-moles	C_2H_2	CO_2	Furan	PhF	C_2H_4	Other
							Products				
—		25	35 2	3 3	(some C_2 and C_4 products on short irradiations)						
C_2H_2	500	30	40 4	23 7							
$CH_3C\ CCH_3$	500	25	40	0 0	10 6						
$CH_3C\ CCH_3$	1000	25	33 5	0 0	19						
$CF_3C\ CCF_3$	500	25		0 5	15 (o bistrifluoromethylbenzene)						
O_2	500	25				0 8	26	1 5			acraldehyde 0 7
$CF_2\ CH_2$	500	30	49 5	1 7					1 0		1 fluorocyclohexa-2 4 diene (small)
$CF_2\ CH_2$	1000	25	39	1 0					1 6		1-fluorocyclohexa 2 4-diene (small)
C_2F_4	500	25	45								o difluorobenzene (*ca* 1)
C_2F_3H	500	25	50	cyclopentadiene 0 13, 1 trifluoromethylcyclopenta 2 4 diene 0 4, *endo* and *exo* 2,2 3-trifluorobicyclo[2 2 0]hex 5 ene 0 9 and 1 3, benzene 0 25, fluorobenzene 1 8 o difluorobenzene 0 38							

The reactivity of cyclobutadiene with respect to mono-olefins was examined using C_2H_4 $C_2F_2H_2$, C_2F_3H, and C_2F_4 With ethylene benzene formation was suppressed but the amounts of volatile products recovered were insufficient for identification The products obtained in the reactions with fluoroethylenes are shown in the Table The highest yield of retrievable products *ca* 21%, was obtained with trifluoroethylene The principal primary products appear to be the *endo*- and *exo*-2,2,3-trifluorobicyclo[2,2 0]hex 5-ene which may be viewed as arising from a 1 2-addition The small amounts of 1-trifluoromethylcyclopenta-2 4-diene could however be a secondary isomerization product Aromatization by HF loss occurs readily but monofluorobenzene formation requires the loss of F_2 which should not be easy Some of the observed products and the low overall yield of the reaction are probably related to the photosensitivity of the primary fluoro-olefin adducts, which may suffer photolysis

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[1] W J R Tyerman M Kato P Kerbarle S Masamune O P Strausz and H E Gunning, *Chem Comm*, 1967 497

[2] W Merk and R Pettit, *J Amer Chem Soc* 1967 **89**, 4787

[3] Preliminary brief descriptions of the apparatus have been given elsewhere,[1] O P Strausz J Font E L Dedio P Kebarle, and H E Gunning *J Amer Chem Soc* 1967 **89** 4805 J Connor G Greig and O P Strausz *ibid* 1969 **91** 5695

[4] From pyrolytic reactions between cyclobutadiene and O_2 at 800° the apparent adduct has been detected *cf* E Hedaya, R D Miller, D W McNeil P F D'Angelo, and P Schissel *J Amer Chem Soc* 1969 **91** 1875

[5] V R Sandel and H H Freedman *J Amer Chem Soc*, 1968 **90** 2059

[6] D L Hufford D S Tarbell and T R Koszalka *J Amer Chem Soc* 1952 **74**, 3014, C Aso and M Miura *J Polymer Sci*., *Part B Polymer Letters* 1966 **4**, 171

[7] S C Barton unpublished results from this laboratory