Photolysis of Tricarbonylcyclobutadieneiron: Evidence for Formation of Free Cyclobutadiene

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FREE cyclobutadiene has not previously been isolated, although there is indirect evidence that it is formed by reaction of ceric ions with tricarbonylcyclobutadieneiron.[1] We now report experiments in which cyclobutadiene was observed directly by kinetic mass spectrometry in flash-photolysed tricarbonylcyclobutadieneiron. The apparatus[2] consists of a conventional flash photolysis cell attached through a small leak to the ion source of an Atlas CH-4 mass spectrometer modified for fast response to transient species. Time-resolved relative-intensity plots were obtained for $m/e = 26$ ($C_2H_2^+$), 52 ($C_4H_4^+$), 78 ($C_6H_6^+$), 104 ($C_8H_8^+$), and 140 [$Fe(CO)_3^+$]. Fe and CO have large peaks in the mass spectrum of the substrate and were not monitored.

With 10—250 millitorr tricarbonylcyclobutadieneiron and 15 torr He, the signal with $m/e = 52$ decayed rapidly in the first 1 or 2 msec. while the benzene and acetylene peaks increased simultaneously and gradually up to *ca.* 5 msec. After this period the intensity ratio, I_{52}/I_{78}, reached a constant value of *ca.* 0·2 corresponding to the mass spectrometric cracking pattern of benzene (Figure). Addition of 10–20 millitorr NO had no significant effect on the product yields indicating that no free radicals are involved in the mechanism. The radical $Fe(CO)_3$ and the cyclobutadiene dimer (C_8H_8) had somewhat longer lives, but they both disappeared in about 20 msec.

The major primary photolytic step must be cyclobutadieneiron tricarbonyl + $h\nu \rightarrow C_4H_4^* + Fe(CO)_3$, which could then be rapidly followed by $C_4H_4^* \rightarrow 2C_2H_2$ and $2C_4H_4^* \rightarrow C_6H_6 + C_2H_2$. The fast decay of the cyclobutadiene in the present experiments may be due to the excess of energy carried over from the photolytic decomposition, since Pettit could distil thermalized cyclobutadiene.[1]

The formation of acetylene and benzene in the continuous photolysis experiments was confirmed by the products being collected and analysed by mass spectroscopy; cyclobutadiene dimer and vinylacetylene (the only known stable C_4H_4 isomer), were not detected. In addition to C_2H_2 and C_6H_6, C_2H_4 and butenes were found. Absorption lines of atomic iron[3] were detected by conventional kinetic spectroscopy after flash photolysis of tricarbonylcyclobutadieneiron but there was no other transient spectrum (6000 > λ > 2300 Å). Supporting evidence that the C_4H_4 species contains an unbranched carbon chain was the formation of furan in an experiment when tricarbonylcyclobutadieneiron was photolysed in the presence of oxygen.

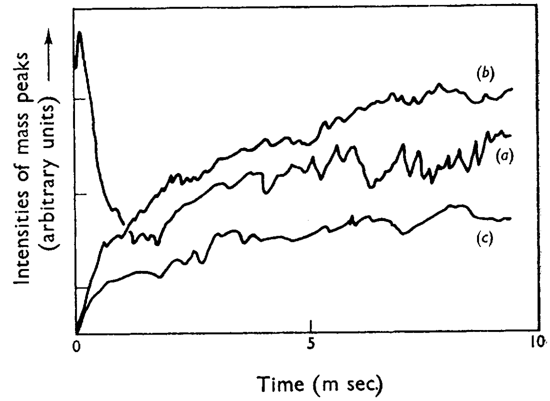

FIGURE. *Variation with time of intensities of mass peaks, from oscillograms.* (a) *cyclobutadiene* (m/e = 52) (*full scale* 0·5 v); (b) *benzene* (m/e = 78) (*full scale* 2 v); (c) *acetylene* (m/e = 26) (*full scale* 2 v). *Photolysis mixture* 10 *millitorr tricarbonylcyclobutaideneiron* + 15 *torr helium.*

Additional support for the formation of cyclobutadiene was obtained from solution phase *in situ* scavenging experiments. An ethereal (50 ml.) solution of tricarbonylcyclobutadieneiron (1 mmole) and dimethyl acetylenedicarboxylate (3 mmoles) was irradated at −20° (with a 450 w Hanovia mercury lamp and Pyrex filter). Silicic acid chromatography of the photolysate gave dimethyl phthalate (17% yield) and traces of dimethyl fumarate. In a second experiment an 18% yield of 2,3-dimethoxycarbonylbicyclo[2,2,0]-hexa-2,5-diene was obtained by Pettit's procedure, and we find that this compound is readily converted into dimethyl phthalate under the conditions stated above. These experiments show that cyclobutadiene can be prepared by photolysis of tricarbonylcyclobutadieneiron, at least as effectively as by ceric ammonium nitrate decomposition.†

Theoretical calculations[4] show that triplet

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† These experiments *by themselves* do not exclude the possibility that the photoexcited tricarbonylcyclobutadieneiron reacts with dimethyl acetylenedicarboxylate prior to the loss of iron carbonyl.

cyclobutadiene is 14—21 kcal./mole higher in energy than the singlet, and this is supported by stereochemical evidence.[5] On the other hand, Skell and Peterson[6] have suggested, also on stereochemical grounds, that tetramethylcyclobutadiene at elevated temperatures behaves as a triplet species. We have therefore photolysed tricarbonylcyclobutadieneiron at 77° K (λ >2200 Å) both pure and in matrices of C_3F_8 and neopentane, and searched for radicals by electron paramagnetic resonance spectroscopy. An intense absorption near $g = 2{\cdot}0$ is attribtued to $Fe(CO)_3$, since it is present also in photolysed $Fe(CO)_5$,[7] supporting our assignment above of the transient mass spectrum at $m/e = 140$ to $Fe(CO)_3^+$. However, no other spectrum was present, which is further evidence that the ground electronic state of cyclobutadiene is a singlet.

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[1] L. Watts, D. Fitzpatrick, and R. Pettit, *J. Amer. Chem. Soc.*, 1965, **87**, 3253.

[2] A preliminary account of the apparatus has appeared: W. J. R. Tyerman, W. B. O'Callaghan, P. Kebarle, O. P. Strausz, and H. E. Gunning, *J. Amer. Chem. Soc.*, 1966, **88**, 4277.

[3] Atomic iron is formed in flash photolysed $Fe(CO)_5$, apparently by stepwise loss of CO molecules, A. B. Callear and R. J. Oldman, *Nature*, 1966, **210**, 730.

[4] M. J. S. Dewar and G. J. Gleicher. *J. Amer. Chem. Soc.*, 1965, **87**, 3255.

[5] L. Watts, D. Fitzpatrick, and R. Pettit, *J. Amer. Chem. Soc.*, 1966, **88**, 623.

[6] P. S. Skell and R. Petersen, *J. Amer. Chem. Soc.*, 1964, **86**, 2530.

[7] W. J. R. Tyerman, O. P. Strausz, and H. E. Gunning, to be published.