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THE REACTION BETWEEN ETHYLENE AND OZONE. A MATRIX STUDY.

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We have undertaken an IR-study of the ethylene-ozone reaction in carbon dioxide and carbon tetrachloride matrices.

The reaction was carried out in a liquid nitrogen cooled cryostat. Matrix gas mixed with ethylene and with ozone was slowly condensed on a cesium iodide window through two separate needle valves (1). About 8 mmoles of carbon dioxide were deposited at 2 x 1 mmole/h. The ethylene and ozone concentrations were varied independently between 0.5 and 2 per cent. The temperature of the cesium iodide window was measured with a platinum resistance thermometer, and could be kept constant anywhere from 65 K to room temperature to within a few hundredths of a degree (2). The matrices were deposited at 65 K. Infrared spectra were recorded on a Perkin- Elmer 180 instrument calibrated with standard gases.

The infrared spectrum of ethylene-ozone in carbon dioxide matrices at 65 K was found to be essentially a superposition of ethylene and ozone spectra. However, the strongest product bands were observable but at least a factor of 2 smaller than expected from a purely statistical model of the distribution in the matrix (3) if nearest neighbours react quantitatively. When the temperature was raised to 77 K, which took about 20 min, the amount of product was increased by an approximate factor of 3. Upon standing at 77 K for about 12 hours the amount of product was somewhat less than doubled, and after 2 hours at 90 K the product band intensity was again doubled. This seems to imply two different reaction rate determining processes at 77 K, the first being a fast reaction of ethylene and ozone molecules already trapped together in the same matrix cage and the second a slow, diffusion controlled process.

At all concentrations used and at all temperatures (4) the relative intensities of all product peaks remained the same. The amount of product varied with ethylene and ozone concentrations as expected for a 1:1 ratio. Comparison with matrix spectra of independently synthesized (5) 1,2,4-trioxolane showed that this was the major product. By warming the cryostat window to 105 K ethylene, ozone and carbon dioxide could all be pumped off leaving the reaction products seemingly unchanged. Upon further warming the products retained their spectral identity although minor changes due to annealing of the solid ozonide phase occurred. At 150-160 K the 1,2,4-trioxolane could be removed, leaving behind a minor product which left the window at 170-180 K. Since all product peaks showed a 1:1 concentration dependence of ethylene and ozone the minor product must also be formed from one ethylene and one ozone molecule. This substance, which is characterized by peaks at 982, 926, 727, 648 and 406 cm^{-1}, seems to be identical to the one Hull et al. associated with the 1,2,3-trioxolane (6). It thus appears as if only two products were formed; in particular no carboxylic or peroxidic species were observed.

From the observed data we can estimate the half-life of a matrix-trapped ethylene-ozone pair to be at least 2 hours at 65 K. The small amount of product observed already at 65 K is probably formed during deposition from ethylene and ozone molecules colliding on the matrix surface before reaching thermal equilibrium. At 77 K the half-life must be less than 15 minutes or we would have observed fairly rapid variations in intensity. This temperature dependence implies an activation energy of 3-5 kcal/mole for the rate determining step. For the gas phase reaction between ethylene and ozone DeMore has reported an activation energy of 4.7 kcal/mole (7).

The formation of 1,2,4-trioxolane is expected from the Criegee mechanism (8). If we assume that this mechanism is the correct one for the reaction in a matrix, and consider the 1:1 stoichiometry, the likely identification of the minor product is 1,2,3-trioxolane. The heat of reaction for the formation of 1,2,3-trioxolane from ethylene and ozone can be estimated to be 40-50 kcal/mole (9) and the activation energy for cleavage of this five-membered ring to be 30 kcal/mole (10). Therefore, freshly formed 1,2,3-trioxolane must transfer 10-20 kcal/mole to the matrix in order to be trapped. In an experiment in a carbon tetrachloride matrix the same product peaks occurred, but the ratio of the minor product : 1,2,4-trioxolane was approximately a factor of 3 lower than in the carbon dioxide matrices. This might be explained as due to a difference in 1,2,3-trioxolane to matrix energy transfer rates.

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References and Notes

(1) L. Fredin, Chemica Scripta, 5, 193 (1974).
(2) L. Fredin, to be published.
(3) R.E. Behringer, J. Chem. Phys., 29, 537 (1958).
(4) At 65 K only the peak at 1073 cm^{-1} could be accurately measured.
(5) C.W. Gillies and R.L. Kuczkowski, J. Amer. Chem. Soc., 94, 6337 (1972).
(6) L.A. Hull, I.C. Hisatsune, and J. Heicklen, J. Amer. Chem. Soc., 94, 4856 (1972).
(7) W.B. DeMore, Int. J. Chem. Kinet., 1, 209 (1969).
(8) (a) R. Criegee, Rec. Chem. Progr., 18, 111 (1957);
(b) R.W. Murray, Acc. Chem. Res., 1, 313 (1968) and references therein.
(9) S.W. Benson, Thermochemical Kinetics, 2nd ed. (John Wiley and Sons, New York, 1976).
(10) H.E. O'Neal and C. Blumstein, Int. J. Chem. Kinet., 5, 397 (1973).