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The Reaction of Carbonylcarbene with Oxygen

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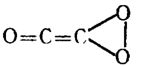
THE discovery that C_2O acts as a carbon-atom donor[1] with many of its reactions similar to those of low-energy free carbon atoms[2] is of interest. Its interaction with oxygen has been studied and used as a reference reaction by Williamson and Bayes.[3] They found that CO and CO_2 were produced in an 8:1 ratio and suggested as possible intermediates.

$O{-}O{-}C{=}C{=}O$

(I)



(II)

Complex (I) will not decompose to CO_2 but complex (II) yields CO_2 incorporating the terminal carbon atom of C_2O. To test these mechanisms we have studied the reaction of end labelled ^{14}CCO with oxygen.

Centre-labelled carbon suboxide was prepared from [2-^{14}C]malonic acid by the method of Mullen and Wolf[4] and purified by preparative v.p.c. using a 20 ft. column of 15% GE SF 96 on Anakrom AB. The purified $^{14}C(CO)_2$ was degassed and stored under liquid nitrogen; contact with mercury was kept to a minimum in order to avoid polymerization of the carbon suboxide. In mixtures with various reactant molecules, the $^{14}C(CO)_2$ was photolyzed using a Hanovia 200 w medium-pressure lamp. Under these conditions only C_2O can be formed and photosensitization does not occur. Both quartz and Pyrex windows were used in the reaction vessel together with a Corning CS 9-54 filter so that the effects of wavelength variation could be studied. Aliquot portions of the reaction mixture were analyzed using standard radio v.p.c. techniques.[5] For CO and CO_2 analysis a 3 ft. silica-gel column was used; hydrocarbon analysis was performed on a 20 ft. 30% dimethylformamide column.

Techniques and procedures were checked by using the well-known reaction of C_2O with ethylene.[1,4,6] Product yields and reactivity, relative to O_2, were found to be as reported. This reaction also served to check the isotopic purity of the $^{14}C(CO)_2$ since in accordance with the reaction sequence

$$^{14}C(CO)_2 = {}^{14}CCO + CO$$
$$H_2C{=}CH_2 + {}^{14}CCO = H_2C{=}{}^{14}C{=}CH_2 + CO$$

no ^{14}CO or $^{14}CO_2$ were produced.

Mixtures of 10 torr $^{14}C(CO)_2$ and 980 torr O_2 were photolyzed in the quartz and Pyrex windowed vessels. In the long-wavelength experiments, using the Pyrex window, the ratio of $^{14}CO_2$: ^{14}CO was $< 0{\cdot}01$, although both unlabelled CO and CO_2 were formed. When shorter wavelengths were used in the photolysis, the ratio of $^{14}CO_2$: ^{14}CO was $0{\cdot}04 \pm 0{\cdot}01$. Even this ratio is in the nature of an upper limit. Irradiation of a mixture of ^{14}CO and O_2 using the quartz window and filter showed that considerable $^{14}CO_2$ was produced by oxidation of ^{14}CO under these conditions.†

The low yield of $^{14}CO_2$ indicates that production of intermediate (II) and decomposition to CO_2 is not an important factor in this system. An

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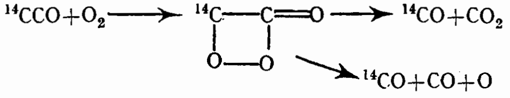
† A mixture of $^{14}C(CO)_2$ and O_2 gave no products on being allowed to stand in darkness.

alternative, consistent with all available data, is a mechanism involving a four-centre complex:



(III)

Intermediate (III) cannot decompose to $^{14}CO_2$. This single complex could also account for the high ratio of $CO:CO_2$ although the present results do not exclude participation by intermediate (I). It seems reasonable to think that complex (II) is not involved, since on theoretical grounds it would appear to be a high-energy configuration. However a four-centre complex such as (III) should have a considerably lower energy. Evidence for end-on complexes such as (I) has been discussed.[7]

The superficial similarity of many of the reactions of C_2O with those of carbon are now well established. With hydrocarbons[1,2] as well as with oxygen, these two species yield many of the same products. Indeed, it is useful to regard C_2O as a prototype of a class of fragment molecules which may be characterized as carbon-atom donors. In systems where both carbon atoms and carbon-atom donors may be present, it becomes difficult to distinguish between their reactions on the basis of product identification alone.‡

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‡ A case in point is the recent work of Martinotti, Welch, and Wolf (*Chem. Comm.*, 1968, 115). CO formed by reaction with O_2 was used as a measure of carbon atom concentration. A number of rather surprising conclusions were reached, including an estimate that bimolecular recombination of carbon atoms occurred at least every fifth collision. The system, formed by microwave decomposition of $^{14}C(CO)_2$ is, however, quite complex. Intervention of carbon-atom donors in the formation of CO is difficult to exclude and may provide an alternate, less startling, explanation of the data.

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