VacuumUltraviolet Photochemistry. III. Formation of Carbon Atoms in the Photolysis of Carbon Suboxide at 1470 Å

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PHOTOLYSIS of carbon suboxide at wavelengths above 2200 Å has been reported by Bayes.[1-3] Based on a heat of formation[4] of C_3O_2 of -25 kcal/mole, it was estimated[3] that it is energetically impossible to form free carbon atoms at these wavelengths and that the reactive intermediate is the C_2O radical.

From the heats of formation of C_3O_2, C(g), and CO and the energies of the excited states of carbon, the minimum energy required to form a carbon atom in the ^3P, ^1D, ^1S states has been calculated and is shown in Table I. It is evident from these calculations that in the photolysis of C_3O_2 at 1470 Å (195 kcal/einstein), it is energetically possible to produce carbon atoms in the ground ^3P state and/or in the ^1D state. If the excited state leading to decomposition of C_3O_2 is a singlet, spin conservation would favor formation of $C(^1D)$. Carbon atoms generated by nuclear transformation[5] react with methane to form ethylene and acetylene. Since photolysis of C_3O_2 in presence of methane at 2537 Å produces ethylene but not acetylene,[1] the formation of carbon atoms in photolysis of C_3O_2 at 1470 Å may be detected by their reaction with methane to form acetylene.

Table I. Wavelengths below which it is energetically possible to produce the indicated carbon atom by the reaction: $C_3O_2 \rightarrow C(g)+2CO$.

State of carbon atom	Energy of state[a] (kcal/mole)	ΔH of reaction (kcal/mole)	Wavelength (Å)
$C(^3P)$	0	143	1998
$C(^1D)$	29	172	1661
$C(^1S)$	62	205	1394

[a] Energies of excited states of carbon are from Natl. Bur. Std. Circ. No. 467 (1949).

We have photolyzed C_3O_2 in the presence of methane ($CH_4/C_3O_2>50$) using the Xe resonance line (1470 Å). The Xe resonance lines (1470 and 1295 Å) were excited in an electrodeless discharge maintained by a Raytheon 2450-Mc/sec microwave generator. A sapphire window eliminates the 1295-Å line. All experiments were performed at 25°C and at a total pressure of 90 mm Hg. After photolysis, samples were analyzed in a Consolidated 21-130 mass spectrometer. Acetylene and ethylene were found to be major products of the photolysis, along with CO. Blank experiments showed that neither acetylene nor ethylene were produced on mixing C_3O_2 and methane for periods comparable to those of the photolyses. In agreement with previous findings,[1] photolysis at 2537 Å did not result in acetylene formation.

There are two explanations for these results:

(I) Carbon atoms are formed in the photolysis of C_3O_2. Insertion of a C atom into a C–H bond of methane results in a highly excited (at least 142 kcal/mole) C_2H_4 molecule. The latter may be quenched by collision or decompose to C_2H_2

$$C_3O_2+h\nu \rightarrow C+2CO, \quad (0)$$
$$C+CH_4 \rightarrow C_2H_4^*, \quad (1)$$
$$C_2H_4^*+M \rightarrow C_2H_4+M, \quad (2)$$
$$C_2H_4^* \rightarrow C_2H_2+H_2. \quad (3)$$

(II) Photolysis at 1470 Å is the same as at 2537 Å[1]

$$C_3O_2+h\nu \rightarrow C_2O+CO, \quad (4)$$
$$C_2O+CH_4 \rightarrow C_2H_4+CO, \quad (5)$$

but secondary photolysis of C_2H_4 occurs resulting in the formation of acetylene:

$$C_2H_4+h\nu \rightarrow C_2H_2+H_2. \quad (6)$$

If (II) occurs to the exclusion of (I), there should be an initial lag in the production of acetylene as ethylene accumulates to a steady-state concentration. No significant decrease in rate of production of acetylene was noted in going from 2% to 0.5% conversion. For longer conversions than 2%, however, it was observed that the rate of production of C_2H_4 decreased, the rate of production of C_2H_2 increased, but the sum of the two rates remained constant. This suggests that, although secondary photolysis of C_2H_4 is not the source of acetylene for shorter conversion experiments, it does make some contribution for longer conversion experiments.

We therefore conclude that carbon atoms are formed in the photolysis of C_3O_2 at 1470 Å and react with methane to form ethylene and acetylene. Further work is in progress.

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