

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

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Citation: *The Journal of Chemical Physics* **43**, 2552 (1965); doi: 10.1063/1.1697160

View online: <http://dx.doi.org/10.1063/1.1697160>

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Arthritis and Metabolic Diseases, and in part by the Advanced Research Projects Agency, Contract SD-68.

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Vacuum-Ultraviolet Photochemistry. III. Formation of Carbon Atoms in the Photolysis of Carbon Suboxide at 1470 Å

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(Received 15 July 1965)

PHOTOLYSIS of carbon suboxide at wavelengths above 2200 Å has been reported by Bayes.¹⁻³ Based on a heat of formation⁴ of C₃O₂ of -25 kcal/mole, it was estimated⁵ that it is energetically impossible to form free carbon atoms at these wavelengths and that the reactive intermediate is the C₂O radical.

From the heats of formation of C₃O₂, 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 C₃O₂ 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 C₃O₂ is a singlet, spin conservation would favor formation of C(¹D). Carbon atoms generated by nuclear transformation⁶ react with methane to form ethylene and acetylene. Since photolysis of C₃O₂ in presence of methane at 2537 Å produces ethylene but not acetylene,¹ the formation of carbon atoms in photolysis of C₃O₂ 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: C₃O₂ → C(g) + 2CO.

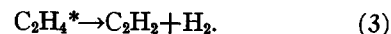
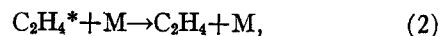
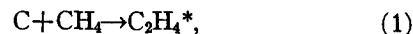
State of carbon atom	Energy of state ^a (kcal/mole)	ΔH of reaction (kcal/mole)	Wavelength (Å)
C(³ P)	0	143	1998
C(¹ D)	29	172	1661
C(¹ S)	62	205	1394

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

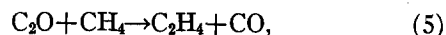
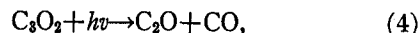
We have photolyzed C₃O₂ in the presence of methane (CH₄/C₃O₂ > 50) using the Xe resonance line (1470 Å). The Xe resonance lines (1470 and 1295 Å) were excited in an electrodeless discharge maintained by a Raytheon 2450-Mc/sec microwave generator. A sapphire window eliminates the 1295-Å line. All experiments 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 C₃O₂ 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:

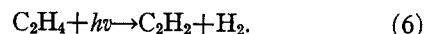
(I) Carbon atoms are formed in the photolysis of C₃O₂. Insertion of a C atom into a C-H bond of methane results in a highly excited (at least 142 kcal/mole) C₂H₄ molecule. The latter may be quenched by collision or decompose to C₂H₂



(II) Photolysis at 1470 Å is the same as at 2537 Å¹



but secondary photolysis of C₂H₄ occurs resulting in the formation of acetylene:



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 C₂H₄ decreased, the rate of production of C₂H₂ increased, but the sum of the two rates remained constant. This suggests that, although secondary photolysis of C₂H₄ 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 C₃O₂ at 1470 Å and react with methane to form ethylene and acetylene. Further work is in progress.

We wish to thank Dr. J. R. McNesby for drawing our attention to this problem.

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