[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, BERKELEY, CALIFORNIA]

Reaction of Oxygen Atoms with Acetylene to Form Ketene

BY IVAN HALLER AND GEORGE C. PIMENTEL

RECEIVED JANUARY 2, 1962

Nitrous oxide, N_2O, was photolyzed at 20°K. in solid argon containing acetylene, C_2H_2, or a mixture of C_2D_2 and C_2HD. The photolysis source was a xenon resonance lamp emitting mainly at 1470 Å. This radiation produces ground state oxygen atoms (^3P). Infrared spectra showed that reaction occurred with C_2H_2 to produce absorption at 2143 cm.$^{-1}$ and with the deuterated acetylenes to produce absorptions at 2142 and 2117 cm.$^{-1}$. The absorptions are assigned to ketene, thus showing that ^3P oxygen atoms can react with acetylene to produce ketene. The activation energy for this reaction is below 8.1 kcal./mole.

Much study has been devoted to the reactions of oxygen atoms in the gas phase.[1-3] Their importance in combustion warrants this attention. DeMore and Davidson[4] have examined the reactions of N_2, O_2, O_3, NO_2 and N_2O with oxygen atoms produced by photolysis of ozone in solid nitrogen. We, too, have investigated a number of the reactions of ground state oxygen atoms by the matrix isolation method.[5] Unique information results since primary reaction products are confined in an inert matrix cage at a very low temperature.[6-8] We report here the reactions of oxygen atoms (^3P) with acetylene in solid argon at 20°K.

Experimental

The cold cell usually used[9] was modified by adding a xenon resonance lamp to the base, as shown in Fig. 1. The Vycor discharge tube was sealed to a LiF window with an epoxy resin and the entire LiF window was then attached to the cold cell base with Apiezon W and with suitable mechanical support.

The discharge tube was excited with a cylindrical resonant cavity (see Fig. 1) coupled to a QK 62 CW tunable magnetron (9.7 cm. wave length). The xenon was introduced to the tube after passing it through a Dry Ice-trichloroethylene trap to remove mercury. Stable operation occurred at 0.10 mm. pressure, and the lamp was evacuated and refilled before each experiment. The average light incident upon the cold cell was estimated to be about 10^{14} quanta per second from the initial rate of photolysis of N_2O (probably a lower limit since unit quantum yield was assumed).

Nitrous oxide, acetylene and argon were mixed at mole ratios $Ar/N_2O = 200$, $N_2O/C_2H_2 \cong 1$. The gas mixture was deposited onto the CsBr cold window (measured temperature, 20° K.) at a rate near 1 cc. (S.T.P.) per minute (45 micromoles of the mixture per minute).

Infrared spectra were recorded after deposition of the sample, after 30 minutes irradiation and again after 2.5 hr. irradiation. Spectra were recorded with a Perkin-Elmer Model 21 spectrophotometer with NaCl optics. The N_2O band in argon (2228 ± 1 cm.$^{-1}$) was used as an internal calibration and frequencies are accurate to ±3 cm.$^{-1}$. The spectral slit width was 7 cm.$^{-1}$ near 2200 cm.$^{-1}$.

The material balance is based on the peak absorption coefficients measured immediately after deposition of a known number of moles of N_2O, C_2H_2 or CH_2CO in solid argon. The material balance is meaningful provided the accommodation coefficients for these three substances are the same since each absorption coefficient is in error by a factor which depends upon the accommodation coefficient and the fraction of the sample condensed on the cold window in the optical path.

Argon (Linde Air Products standard grade) was passed over copper filings at 600° and then through a coil immersed in liquid nitrogen. Acetylene (Matheson, 99.5%) was purified by two bulb-to-bulb distillations, discarding first and last fractions. Deuterated acetylene was prepared by reaction of D_2O with CaC_2 (Coleman and Bell) and purified by three bulb-to-bulb distillations. The sample was estimated to contain 78% C_2D_2 and 21% C_2HD from the intensities of the ν_3 bands of C_2D_2 and C_2HD, respectively, 2418 and 2552 cm.$^{-1}$ in solid argon. The ratio of the absorption coefficients was assumed to be $\nu_3(C_2D_2)/\nu_3(C_2HD) = 1.6$, the same as in the gas phase.[10]

Ketene was prepared by the pyrolysis of acetone vapor on chromel wire at a dull red heat. Acetone (Brothers Chemical Company, Reagent Grade) was refluxed over the hot wire, and the volatile products were collected in an acetone solution at −80°. The product was distilled at atmospheric pressure, accepting the fraction boiling under 40°. This fraction was purified by three bulb-to-bulb distillations.

Results

Nitrous oxide was photolyzed in one experiment in the presence of C_2H_2 and in another experiment in the presence of the deuteriated acetylenes, C_2D_2 and C_2HD. Figure 2a shows spectra from the C_2H_2 experiment before photolysis (dotted line), after 30 minutes photolysis (dashed line) and after 2.5 hr. photolysis (solid line). Figure 2b shows the same information for the C_2D_2–C_2HD experiment. The intensities, measured with a reproducibility of ±0.005 in the optical density, are recorded in Table I.

TABLE I

OPTICAL DENSITIES OF SPECTRAL FEATURES DURING PHOTOLYSIS OF N_2O AND ACETYLENE IN SOLID ARGON

ν (cm.$^{-1}$)	Photolysis time 0	30 min.	150 min.	Micromoles change at 150 min.	Identity
		C_2H_2 experiment			
2228	0.695	0.664	0.628	−1.7 ± 0.4	N_2O
740	.450	.414	.390	−2.3 ± 0.5	C_2H_2
2143	.000	.020	.036		CH_2CO
		C_2D_2–C_2HD experiment			
2228	0.686	...	0.605	−2.0 ± 0.4	N_2O
2552	.025	...	.017	−1.1 ± .9	C_2HD
2418	.150	...	.130	−1.6 ± .6	C_2D_2
2142	.000	...	.010		CHDCO
2117	.000	...	.013		CD_2CO

---

(1) E. W. R. Steacie, "Atomic and Free Radical Reactions," Reinhold Co., New York, N. Y., 1954.

(2) S. Sato and R. J. Cvetanovic, *Can. J. Chem.*, **36**, 279, 970, 1668 (1958); R. J. Cvetanovic, *J. Chem. Phys.*, **23**, 1375 (1955); *ibid.*, **33**, 1063 (1960).

(3) L. I. Avramenko and R. V. Lorentso, *Zhur. Fiz. Khim.*, **26**, 1084 (1952).

(4) W. B. DeMore and N. Davidson, *J. Am. Chem. Soc.*, **81**, 5869 (1959).

(5) I. Haller, Ph.D. Thesis, University of California, Berkeley, (1961). Reactions with C_2H_4, CO and NO also were studied.

(6) G. C. Pimentel, *J. Am. Chem. Soc.*, **80**, 62 (1958).

(7) H. W. Brown and G. C. Pimentel, *J. Chem. Phys.*, **29**, 883 (1958).

(8) C. D. Bass and G. C. Pimentel, *J. Am. Chem. Soc.*, **83**, 3754 (1961).

(9) E. D. Becker and G. C. Pimentel, *J. Chem. Phys.*, **25**, 224 (1956).

(10) D. F. Eggers, Jr., I. C. Hisatsune and L. Van Alten, *J. Phys. Chem.*, **59**, 1124 (1955).

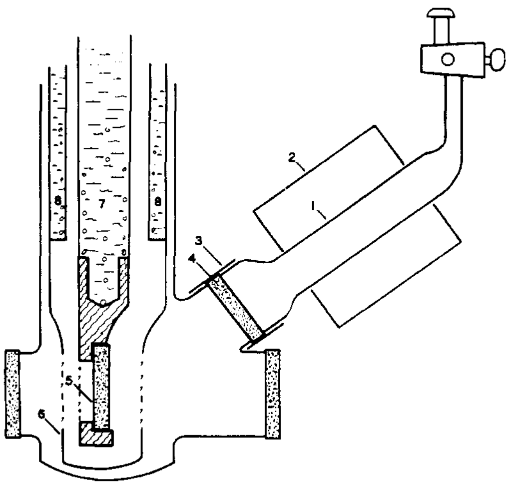


Fig. 1.—Microwave-powered xenon lamp: 1, 25 mm. Vycor tube; 2, resonant cavity; 3, glass tube; 4, LiF window; 5, CsBr window; 6, radiation shield; 7, liquid hydrogen; 8, liquid nitrogen.

For identification, ketene was suspended in solid argon. Absorptions were observed at 2142 and at 1373 ± 1 cm.$^{-1}$ and with the former line (2142 cm.$^{-1}$) more intense by a factor of 4.2.

Discussion

Zelikoff and Aschenbrand[11] determined the primary reaction in the photolysis of gaseous N_2O with light of wave length 1470 Å. to be reaction

$$N_2O + h\nu\ (1470\ \text{Å.}) \longrightarrow N_2(A^3\Sigma) + O(^3P) \quad (1)$$

With light of wave length 1236 Å., the primary reaction proceeds by a dual mechanism.

$$N_2O + h\nu\ (1236\ \text{Å.}) \longrightarrow N_2(B^3\Pi) + O(^3P) \quad (2)$$

$$N_2O + h\nu\ (1236\ \text{Å.}) \longrightarrow NO(^2\Sigma) + N(^4S) \quad (3)$$

A xenon lamp emits two intense lines at 1470 and 1295 Å. and many weak lines in the visible and near ultraviolet. Faltings, *et al.*,[12] estimated the peak intensity ratio I(1470 Å.)/I(1295 Å.) to be three. Tanaka and Zelikoff[13] found this ratio to be pressure dependent since the line at 1470 Å. is pressure broadened whereas the 1295 Å. line is not. There is no evidence of interference in the present study by the products from reaction 3.

From the heats of formation of N_2O (20.31 kcal./mole at 0°K.),[14] the heat of formation of (^3P) oxygen atoms (58.59 kcal./mole),[14] the excitation energies of the nitrogen $A^3\Sigma$ state (143.51 kcal./mole)[15] and $B^3\Pi$ state (170.44 kcal./mole), and the energies of the quanta (1470 Å. gives 194.5 kcal./mole and 1295 Å. gives 220.6 kcal./mole), we calculate the excess energies of the products. In reaction 1 the products divide 12.7 kcal./mole of excess energy whereas in reaction 2 the products divide 11.9 kcal./mole.

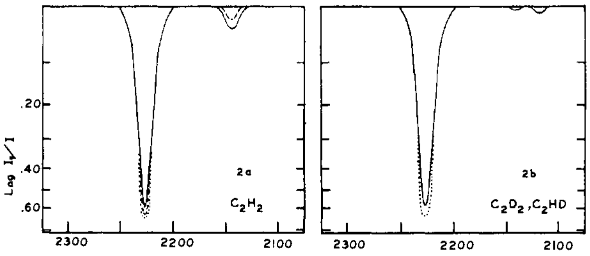


Fig. 2.—Infrared spectra of N_2O and acetylene in argon: ......, before photolysis; --------, 30 min. photolysis; ———, 150 min. photolysis.

The bands appearing during photolysis can be assigned with confidence to ketene. Table II compares the absorptions produced by the photolysis products to the absorptions of CH_2CO in argon matrix and of CH_2CO, CHDCO and CD_2CO in the gaseous state. The frequency differences, gas—matrix, leave no doubt concerning the identification.

TABLE II

COMPARISON OF SPECTRA OF GASEOUS KETENES TO MATRIX SPECTRA

Gas phase[16] Species	ν(cm.$^{-1}$)	CH_2CO in solid argon ν(cm.$^{-1}$)	N_2O–C_2H_2 expt. ν(cm.$^{-1}$)	N_2O–C_2D_2–C_2HD expt. ν(cm.$^{-1}$)
CH_2CO	2151	2141.8	2143	..
CHDCO	2150	....	..	2142
CD_2CO	2121	....	..	2117

The absorption coefficient of acetylene at 1470 Å. is relatively low,[17] and we feel that the photolysis of acetylene is not important in our experiments. We attribute the formation of ketene to the reaction of oxygen atoms (^3P) with acetylene. The oxygen atoms have at most, 8.10 kcal./mole of excitation (the energy they would have if all of the excess energy in reaction 1 is divided as translational energy). This estimate of the maximum energy of the oxygen atoms places an upper limit on the activation energy for

$$O^*(^3P) + C_2H_2 \longrightarrow CH_2CO \quad \Delta H^{\ddagger} < 8.1\ \text{kcal./mole} \quad (4)$$

Ketene has been reported as a product of the controlled oxidation of acetylene,[18] but there has been no direct evidence that it could be formed by reaction 4. Harteck and Kopsch[19] found that the main products of the reaction of gaseous acetylene with oxygen atoms prepared in a discharge through O_2 are H_2O, CO_2 and H_2. They concluded the activation energy for reaction is not greater than 4 kcal. Geib and Harteck[20] observed an addition product when oxygen atoms from a discharge and acetylene are allowed to react as they impinge on a cold surface at the temperature of liquid oxygen. The addition product was assigned the formula $C_2H_2O_2$ on the basis of the material balance after warming. Geib and Harteck suggest the structure

---

(11) M. Zelikoff and L. M. Aschenbrand, *J. Chem. Phys.*, **22**, 1680 (1954); *ibid.*, **27**, 123 (1957).

(12) K. Faltings, W. Groth and P. Harteck, *Z. Physik. Chem.*, **B41**, 15 (1938).

(13) K. Tanaka and M. Zelikoff, *J. Opt. Soc. Am.*, **44**, 254 (1954).

(14) F. D. Rossini, "Selected Values of Chemical Thermodynamic Properties," N.B.S. Circular No. 500 (1961).

(15) G. Herzberg, "Molecular Spectra and Molecular Structure," Vol. I, Van Nostrand Co., New York, N. Y., 1950, p. 552.

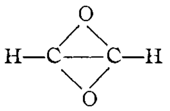
(16) W. F. Arendale and W. H. Fletcher, *J. Chem. Phys.*, **26**, 793 (1957).

(17) G. Moe and A. B. F. Duncan, *J. Am. Chem. Soc.*, **74**, 3136 (1952).

(18) E. H. Ingold, *J. Chem. Soc.*, **125**, 1534 (1924).

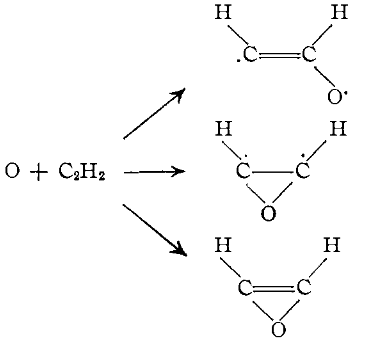
(19) P. Harteck and V. Kopsch, *Z. physik. Chem.*, **B12**, 327 (1931).

(20) K. H. Geib and P. Harteck, *Trans. Faraday Soc.*, **30**, 133 (1934); *Ber.*, **66B**, 1815 (1933).



The products found upon warming were glyoxal, CO, HCOOH, H_2O and CO_2. Ketene was not identified.

We propose that reaction 4 occurs in two steps, oxygen atom addition, (5) followed by isomerization (6). Three possible structures for the addition are

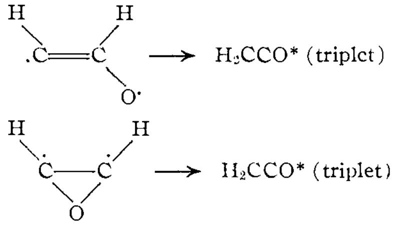


(5)

(5′)

(5″)

Since product 5″ does not conserve spin, products 5 and 5′ are favored. Either could isomerize to a



(6)

(6′)

triplet state of ketene followed by phosphorescence of the excited ketene. No such low triplet state of ketene is known, however.

Acknowledgments.—We thank Dr. B. H. Mahan for valuable advice in the design of the light source. One of us (I.H.) gratefully acknowledges fellowship aid from Texaco, Inc., during 1959–1960. We further acknowledge research support by the American Petroleum Institute Research Project 54 and the United States Air Force through AFOSR of the Air Research and Development Command.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY, STANFORD, CALIF.]

On the Morphology of the Crystalline State in Polymers

BY P. J. FLORY

RECEIVED JANUARY 16, 1962

Geometrical and spatial requirements for the accommodation of polymer chains in random conformations set an upper limit of $v_2\, A_c/2A_a$ on the fraction of those chains emerging from the face of a lamellar crystallite of large lateral dimensions which may traverse the interfacial zone and vanish into the surrounding disordered region without returning to the crystallite; v_2 is the volume fraction of polymer in the surrounding phase and A_a and A_c are the cross sections occupied by the polymer chain in its amorphous and crystalline conformations, respectively. A considerable fraction of the chains emanating from the crystal face may nevertheless escape the environs of the crystal without returning to it (for $v_2 \sim 1$). Those which return need not adopt the regularly folded pattern currently assumed. Helical conformations, such as occur among biological polymers, increase the crystalline chain cross section and thus alleviate the crowding of chains otherwise attending their disorientation. The spatial factors enforcing re-entry of emerging chains become operative only when the transverse dimensions of the crystal are large. The cross sections of both primary and secondary nuclei are sufficiently small to permit their formation from bundles of separate ("unfolded") chain molecules. In copolymers, the infrequency of occurrence of long runs of the crystallizing unit generally precludes multiple participation (*i.e.*, "folding") of the same molecule in a given crystallite. Hence, the lamellar morphology characteristic of homopolymers may of necessity be supplanted by crystallites of small lateral dimensions (assuming $A_c/A_a < 2$). For similar reasons, crystallites generated by stretching must be restricted in their lateral dimensions owing to the incompatibility of any sort of folded arrangement with the axial orientation imposed by deformation. The presence of disorganized interfacial layers on lamellar crystallites separating from a dilute solution may diminish their stability perceptibly largely due to osmotic forces tending to disperse these relatively concentrated amorphous layers. At equilibrium with a dilute solution the regularly folded array offers the greatest stability. It is suggested however that the morphology which develops during crystallization is determined by kinetic factors which preclude achievement of this optimum result. The elementary process in crystallite growth is considered to consist in the (reversible) deposition of a chain unit rather than of an entire sequence of units. Mobility of chains in the outermost layer of the growing crystal face is viewed as a factor of importance.

I. Introduction

The discovery of the characteristic single crystal habit of the platelets precipitated from dilute solutions of linear polymers has stimulated unprecedented interest in the morphology of the crystalline state in polymers.[1–7] The thicknesses of these platelets, or lamellae, range from 70 to 200 Å. units; they may measure up to several microns in transverse dimensions. Crystalline overgrowth layers of the same thickness frequently occur, depending on the conditions attending crystallization. The patterns frequently displayed by these layers conform to the requisites for accretion by screw dislocation mechanisms. Most

---

(1) K. H. Storks, *J. Am. Chem. Soc.*, **60**, 1753 (1938).

(2) R. Jaccodine, *Nature*, **176**, 301 (1955).

(3) P. H. Till, *J. Polymer Sci.*, **24**, 301 (1957).

(4) A. Keller, *Phil. Mag.* [8], **2**, 1171 (1957). A. Keller and A. O'Connor, *Discussions Faraday Soc.*, **25**, 114 (1958). A. Keller, "Growth and Perfection of Crystals," Ed. by R. H. Doremus, B. W. Roberts and D. Turnbull, John Wiley and Sons, Inc., New York, N. Y., 1958, pp. 499–528.

(5) E. W. Fischer, *Z. Naturforsch.*, **12a**, 753 (1957). R. Eppe, E. W. Fischer and H. A. Stuart, *J. Polymer Sci.*, **34**, 721 (1959).

(6) P. H. Geil, *ibid.*, **44**, 449 (1960); *ibid.*, **47**, 65 (1960); *ibid.*, **51**, S10 (1961).

(7) B. G. Ranby, F. F. Morehead and N. M. Walter, *ibid.*, **44**, 349 (1960).