

9.13 and 8.25 τ ; infrared: $>C=C<$ 8165 cm.^{-1}).^{2,3}

As to the mechanism of the reaction, formation of chlorocarbene from methylene chloride and I is likely to be the first step.⁴ As a strongly nucleophilic reagent, I can be visualized to combine with the carbene by either of two ways: path (a) assumes electrophilic addition of the carbene to the π -electrons of the double bond, generating intermediate II which gives V *via* β -elimination. Or, the carbene may attack the incipient vinylcarbanion to form intermediate III, (path b), which generates vinylcarbene IV by α -elimination.⁵ Cyclization of the latter by rotation of the *gem* dimethyl group through 90° will lead to the cyclopropene V. The subsequent replacement of the olefinic proton in V by lithium occurs on reaction with strongly basic I. The resulting cyclopropenyllithium compound VI is also formed when V is allowed to react with methyllithium in tetrahydrofuran at 0°.

This increased acidity of the olefinic proton in cyclopropenes has been predicted from theoretical considerations^{6,7} which attribute a high degree of s-character to the C—H bond because of the large "ring strain." Deuterium exchange work on short-lived cyclopropene intermediates supports this concept.⁷ Additional indication of the correctness of the theory is given by the increased acidity of VII (pK_a 3.7) when compared with other α,β -unsaturated carboxylic acids.

The reaction is being extended at the present time to the introduction of other functional groups in the 1-position of cyclopropenes. A detailed investigation of the mechanism is also in progress.

(2) Other 1,2-dialkyl-substituted cyclopropenes are reported to exhibit C=C stretching vibration in the same region: P. K. Faure and J. C. Smith, *J. Chem. Soc.*, 1818 (1956); W. v. E. Doering and T. Mole, *Tetrahedron*, **10**, 65 (1960).

(3) It may be of interest to point out the unusually large shift in the C=C stretching frequency (110 cm.^{-1}) of the cyclopropene ring system caused by introduction of a second alkyl substituent on the double bond.

(4) G. L. Closs and L. E. Closs, *J. Am. Chem. Soc.*, **82**, 5723 (1960).

(5) For the equivalent mechanism of the reaction of chlorocarbene with alkyllithium compounds see: G. L. Closs, Abstracts of Papers of the 138th Meeting of the American Chemical Society, New York, N. Y., September, 1960, p. 9-P.

(6) A. D. Walsh, *Trans. Faraday Soc.*, **45**, 179 (1949).

(7) K. B. Wiberg, R. K. Barnes and J. Albin, *J. Am. Chem. Soc.*, **79**, 4994 (1957).

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RECEIVED DECEMBER 13, 1960

A NEW FLUORIDE OF OXYGEN—O₄F₂¹

Sir:

The preparation and properties of pure ozone fluoride, or O₃F₂, were described recently.^{2,3,4} It has now been established that the elusive O₄F₂^{2,3} also can be obtained. As in the case of O₂F₂ and O₃F₂, it is produced by an electrical discharge at low

(1) This research was financed at first, in part, by the Army Ballistic Missile Agency, Redstone Arsenal, Huntsville, Alabama, and at present by the Department of the Navy, Office of Naval Research.

(2) A. D. Kirshenbaum and A. V. Grosse, *J. Am. Chem. Soc.*, **81**, 1277 (1959), see there for previous literature.

(3) A. D. Kirshenbaum, J. G. Aston and A. V. Grosse, *Final Report*, Contract No. DA-36-034-ORD-2250, Nov. 18, 1958.

(4) A. D. Kirshenbaum, A. V. Grosse and J. G. Aston, *J. Am. Chem. Soc.*, **81**, 6398 (1959).

temperatures and pressures by using a mixture of 2 moles O₂ to 1 mole F₂, by cooling more effectively and to lower temperatures, *i.e.*, 60–77°K. (instead of 90°K.), and using less power in the discharge (*i.e.*, 4.5–4.8 milliamp at 840–1280 volts as against 20–30 ma. at 2000–3000 v.).

At 77°K. O₄F₂ is a reddish brown *solid*, depositing on the glass walls of the discharge vessel between the electrodes. It differs in color from O₃F₂, and sometimes forms clusters of long needle-like brown crystals.

O₄F₂ has a vapor pressure of less than 1 mm. at 90°K. It is a liquid and stable, at least for a couple of hours, at 90°K., since no noticeable rise in pressure occurs. Between 90 and 110°K. it decomposes slowly into O₃F₂ and O₂, and the latter at 110°K. to O₂ and O₂F₂. Since O₂F₂ in turn forms O₂ + F₂ at about 200°K. the whole O₄F₂ is decomposed into O₂ and F₂ gas.

The composition of O₄F₂ was established both by (a) synthesis and (b) analysis. In a synthetic case 355 cm.^3 (at S.T.P.), of a 2.05 \pm 0.03:1 O₂/F₂ mixture reacted at 77°K. in a discharge vessel described previously.^{1,2} The gases were admitted at a rate of 2.0 $\text{cm.}^3/\text{min.}$ (S.T.P.); the pressure was 5–15 mm. and the current 4.5 to 4.8 milliamp. at 840–1280 volts. All of the mixture was converted quantitatively to the solid reaction product, except for 15.4 cm.^3 of gas, which was pumped off periodically in order to keep the gas phase composition constant. Even assuming these 15.4 cm.^3 to be pure O₂, the composition of the product should equal O_{4.00}F_{2.06}.

Typical analyses of the gas produced from the solid product, using a Moissan mercury absorption buret for F₂ and an Orsat apparatus for O₂, are: 96.9 cm.^3 (at S.T.P.) contained 66.3 mole % O₂ and 33.7 mole % F₂, ratio O₂:F₂ = 1.95 \pm 0.03; 55.6 cm.^3 gas (at S.T.P.) gave 66.5 mole % O₂ and 33.4 mole % F₂, ratio O₂:F₂ = 1.98 \pm 0.05%. Theoretical for O₄F₂ is 2.00.

The vapor pressures of O₃F₂, O₂F₂ and O₂ differ widely and any O₂ present can be pumped off easily; thus the elementary composition O₄F₂ cannot be due to dissolved O₂. The proof that it is *not* due to O₃ is more difficult. This proof is necessary, however, because O₂ gas alone, under the pressure, temperature and discharge conditions, is converted into liquid or solid O₃. Furthermore, liquid O₃ and liquid O₃F₂ mix homogeneously in any proportion at 90°K., and the O₃ + 3O₃F₂ mixture, on cooling to 77°K., forms a brown mass very similar in appearance to O₄F₂. Attempts to distinguish O₄F₂ from the O₃ + O₃F₂ mixtures by visible spectra could not be made because the molecular extinction coefficients for O₃F₂ and O₄F₂ were not known.

It occurred to us that a simple differentiation could be provided by the solubility behavior of the compounds in liquid O₂. It was found that our samples (0.7–1.0 g.) of O₄F₂, extracted at 77°K. by condensation of liquid O₂ (\approx 25 cc.), gave no visible trace of O₃. On analysis this particular sample, after liquid O₂ extraction and pumping off all O₂, had the composition O_{4.00}F_{2.04}. In contrast, the O₃ + 3O₃F₂ mixture prepared from pure O₃ and O₃F₂, immediately gave a deep blue extract of O₃ in O₂.