acetic acid system (3:2:5) at an approximate K value of 1.04; $[\alpha]^{21}\text{D}$ $-54.0°$ (c 1, 1 N acetic acid). *Anal. Calcd.* for $C_{43}H_{65}N_{11}O_{12}SSe$: C, 49.7; H, 6.31; N, 14.8. Found: C, 49.6; H, 6.50; N, 14.6. The deamino-6-seleno-oxytocin was indistinguishable from deamino-oxytocin[3] upon thin-layer chromatography and gel filtration under the conditions described for 6-seleno-oxytocin.

Upon bioassay 6-seleno-oxytocin was found to possess approximately 420 units/mg. of oxytocic activity,[10] 400 units/mg. of avian vasodepressor activity,[11] 400 units/mg. of milk-ejecting activity,[12] and 4 units/mg. of pressor activity.[13] The deamino-6-seleno-oxytocin was found to possess approximately 500 units/mg. of oxytocic activity, 620 units/mg. of avian vasodepressor activity, 400 units/mg. of milk-ejecting activity, and 1 unit/mg. of pressor activity. Thus the replacement of sulfur by selenium in the 6 position yields highly potent isologs of oxytocin and deamino-oxytocin although they are somewhat lower in potency than the hormone itself and its comparable deamino analog. The results also show that with 6-seleno-oxytocin, which is practically isosteric with oxytocin, the replacement of the free amino group by hydrogen enhances the oxytocic and avian vasodepressor activities and lowers the pressor activity as it does in the case of oxytocin.[14]

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(10) Oxytocic assays were performed according to the method of Holton (*Brit. J. Pharmacol.*, **3**, 328 (1948)) on uteri from rats in natural estrus with the use of magnesium-free van Dyke–Hastings solution as employed by Munsick (*Endocrinology*, **66**, 451 (1960)).

(11) R. A. Munsick, W. H. Sawyer, and H. B. van Dyke, *ibid.*, **66**, 860 (1960).

(12) H. B. van Dyke, K. Adamsons, Jr., and S. L. Engel, *Recent Progr. Hormone Res.*, **11**, 1 (1955); W. Y. Chan, *J. Pharmacol.*, **147**, 48 (1965).

(13) "The Pharmacopeia of the United States of America," 16th Revision, Mack Printing Co., Easton, Pa., 1960, p. 793.

(14) W. Y. Chan and V. du Vigneaud, *Endocrinology*, **71**, 977 (1962).

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The Vibrational State of Hydroxyl Radicals Produced by Flash Photolysis of a Water–Ozone–Argon Mixture

Sir:

A number of gas phase reactions of the general type[1]

$$A + BCD \longrightarrow AB + CD + \Delta H \qquad (1)$$

are known in which the products are formed with excess vibrational energy. The generalization has been made that "the molecule AB with the newly formed bond, may take a high proportion of the exothermic energy of reaction in the form of unequilibrated vibrational energy."[1] Only two experiments have been performed in which the state of the CD molecule was observed.

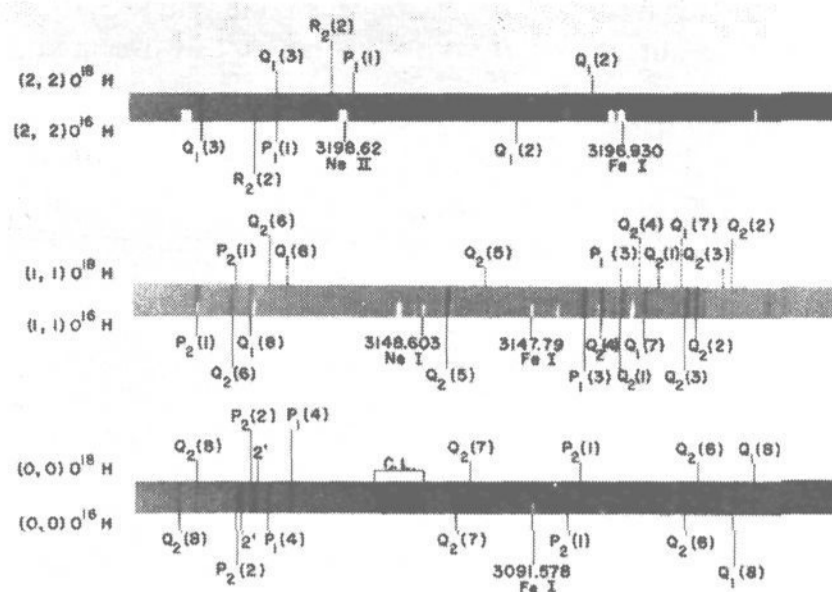(1) R. G. W. Norrish, *Inst. Intern. Chim. Solvay, Conseil Chim.*, **12**, 99 (1964).

Figure 1. Absorption spectra from flash photolysis of ozone–water(O^{18})–argon mixture.

A study of reaction 2^2 by flash photolysis and absorption

$$Cl + ClNO \longrightarrow Cl_2 + NO + 20 \text{ kcal.} \qquad (2)$$

spectroscopy has shown the absence of vibrationally excited NO, but no attempt was made to observe excited Cl_2. An infrared emission experiment in the flow system

$$H + ClNO \longrightarrow HCl + NO + 65 \text{ kcal.} \qquad (3)$$

has shown the presence of vibrationally excited HCl, but the concentration of excited NO was below the limit of detectability.[3]

This communication deals with the reaction[4]

$$O(^1D) + H_2O \longrightarrow OH + OH + 29 \text{ kcal.} \qquad (4)$$
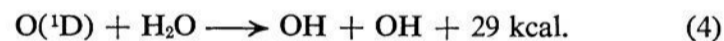
in which the products are identical and the new bond must be distinguished by isotopic labeling. It is also unlike reactions 2 and 3 in that it must involve conversion of electronic energy of a reactant to vibrational energy of a product, since reaction 4 with ground-state $O(^3P)$ atoms is endothermic by 16 kcal. The $O(^1D)$ was generated by the flash photolysis of ozone in the ultraviolet. The water vapor mixed with the ozone was highly enriched in O^{18}. The OH was observed in the near-ultraviolet band system and the small isotope shift was used to distinguish between the old and the new OH bonds.

The annular flash photolysis system used here will be described in a later publication. The 1000-joule photolysis flash lamp gave a light pulse of about 10-μsec. duration. The effective path length through the photolyzed gas was 180 cm. Absorption spectra were obtained with a quartz capillary flash lamp. The plane grating vacuum spectrograph used here[5] has a resolution greater than 300,000 and a reciprocal dispersion of 0.15 Å./mm.

(2) N. Basco and R. G. W. Norrish, *Proc. Roy. Soc.* (London), **A268**, 291 (1962).

(3) J. K. Cashion and J. C. Polanyi, *J. Chem. Phys.*, **35**, 600 (1961); P. E. Charters, B. N. Khare, and J. C. Polanyi, *Discussions Faraday Soc.*, **33**, 276 (1962).

(4) W. D. McGrath and R. G. W. Norrish, *Proc. Roy. Soc.* (London), **A254**, 317 (1960); N. Basco and R. G. W. Norrish, *ibid.*, **A260**, 293 (1961).

(5) P. E. Rouse, Jr., D. L. Upham, R. Engleman, Jr., and H. M. Peek, to be published.

Mixtures were made containing one part of 95% oxygen-18 enriched water vapor, one part of ozone, and eight parts of argon. The photolysis cell was filled with 10 torr of this mixture for each exposure. The effective exposure time was about 15 μsec. directly following the photolysis flash. A number of spectra in the hydroxyl absorption bands between 3060 and 3300 Å. were taken using flash photolysis and this gas mixture.

Figure 1 shows three small sections of the hydroxyl spectrum. The bottom spectrum is about 6 Å. of the (0,0) band around 3090 Å. Both $O^{18}H$ and $O^{16}H$ are strong and approximately equal in intensity in the (0,0) band. The isotope shift is about 0.1 Å. The section labeled C.L. is an artifact of the spectrograph.

The middle spectrum is in the (1,1) band around 3148 Å. The $O^{16}H$ spectrum is strong, but only at the calculated positions (dotted lines above spectrum) of the strongest $O^{18}H$ lines is there any indication of absorption, for example at the $Q_2(3)$ and $Q_2(2)$. It is estimated that the ratio $O^{18}H$ ($v'' = 1$)/$O^{16}H$ ($v'' = 1$) is around 10^{-2}. This is somewhat more than expected on the basis of the 0.2% natural abundance of O^{18}.

The top spectrum is in the (2,2) band around 3197 Å. The $O^{16}H$ spectrum is fairly strong, but no $O^{18}H$ was detected at the calculated positions. The sensitivity for detecting $O^{18}H$ in the (2,2) band is not as high as it is in the (1,1) band.

No evidence for OH of either isotope was found at the location of the (3,3) band. This result has been obtained before,[4] but the sensitivity in the present high resolution experiments is thought to be considerably greater. The $v'' = 3$ state of OH corresponds to 29.2 kcal., or slightly more than the exothermicity of reaction 4. Some highly excited oxygen molecules from the oxygen atom–ozone side reaction were detected in the Schumann–Runge absorption band system. Both the hydroxyl and oxygen molecular spectra had rotational distributions and line widths consistent with approximately room temperature.

The most important conclusion of this study is that the newly formed OH bond receives most of the available vibrational energy, while the old OH bond remains vibrationally cold. This result is not too unexpected since the OH bond length in water is almost identical with that in the free OH radical. While no absolute measurements of OH concentrations have been made, it appears that about one out of six radicals coming from reaction 4 is vibrationally excited. The vibrational energy exchange process

$$O^{16}H^* + O^{18}H \rightarrow O^{16}H + O^{18}H^*$$
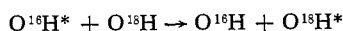
is slow under the conditions of these experiments.

Further studies of (4) and similar reactions are in progress.

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Facile Addition of a Grignard Reagent to an Unconjugated Ethylenic Linkage

Sir:

Despite their pronounced ability to add to diverse unsaturated organic compounds, Grignard reagents hitherto have not been found to add across unconjugated carbon–carbon multiple bonds. Only in the case of ethylenic linkages conjugated with carbonyl or related groups[1] or of the exocyclic ethylenic linkage in substituted fulvenes[2] have additions of Grignard reagents to olefinic linkages been well substantiated. Occasional reports of successful Grignard additions to ordinary ethylenic or acetylenic linkages have been discredited subsequently by the careful investigations of Gilman and co-workers.[3] In the light of previous work, therefore, we were surprised recently to observe the smooth addition of a Grignard reagent to an unconjugated ethylenic linkage. To our knowedge, this constitutes the first authenticated case of such a Grignard addition. Moreover, since appealing extensions of this type of reaction to other systems appear possible, we wish to put forward our findings at this time.

In the preparation of allyldiphenylcarbinol (I) by the interaction of benzophenone with allylmagnesium bromide in ethyl ether,[4] we obtained both I (70–75%) and a new carbinol II (10–20%, b.p. 160° (0.5 mm.)). Both carbinols were dehydrated in individual runs by heating their benzene solutions with traces of p-toluenesulfonic acid. As anticipated, allyldiphenylcarbinol (I) yielded 1,1-diphenyl-1,3-butadiene (III).[5] The new carbinol II, however, gave a hydrocarbon (b.p. 130° (0.4 mm.)) which proved to be 1,1-diphenyl-1,6-heptadiene (IV). The structure of IV is supported by the following data: (a) elemental analysis (*Anal.* Calcd. for $C_{19}H_{20}$: C, 91.88; H, 8.12. Found: C, 91.83; H, 8.01); (b) oxidation with hot $KMnO_4$ to yield benzophenone; (c) infrared spectrum (bands (cm.$^{-1}$) at 1650 (C=C), 1610 and 1585 (C=C conjugated with phenyl), 910 and 990 (CH=CH$_2$), and 695 and 760 (C$_6$H$_5$)); (d) n.m.r. spectrum in CCl$_4$ (peaks [δ in p.p.m. (integrated areas)] at 7.22 (10.0, phenyl), triplet at 6.06 ($J = 8$ c.p.s.), and multiplets between 4.7 and 6.0 (total vinyl of 4.1), multiplets at 2.04 (4.0) and at 1.5 (2.1)); and (e) ultraviolet spectrum in cyclohexane (λ_{max} 250 mμ (log ϵ 2.13); 1,1-diphenyl-1-butene has λ_{max} 251 mμ). Accordingly, the structure of the new carbinol II as 1,1-diphenyl-6-hepten-1-ol can be deduced from its spectral properties [*e.g.*, infrared spectral bands (cm.$^{-1}$) at 3600 (OH), 1645 (C=C), 1600 (aromatic C=C), and 910 and 990 (CH=CH$_2$)] and from its smooth dehydration to form 1,1-diphenyl-1,6-heptadiene. The foregoing reactions are summarized in Chart I.

In considering the origin of the interesting carbinol II, the question arises whether the benzophenone need

(1) R. C. Fuson, *Advan. Organometal. Chem.*, **1**, 221 (1964).

(2) *Cf.* R. C. Fuson and O. York, Jr., *J. Org. Chem.*, **18**, 570 (1953), for leading references.

(3) (a) *Cf.*, *inter alia*, H. Gilman and J. H. McGlumphy, *Rec. trav. chim.*, **47**, 418 (1928). (b) M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Nonmetallic Substances," Prentice-Hall, Inc., New York, N. Y., 1954, pp. 87–90, presents a precis of previous literature.

(4) M. S. Kharasch and O. Weinhouse, *J. Org. Chem.*, **1**, 209 (1936).

(5) All compounds involved in this study were characterized by satisfactory spectroscopic and analytical data. *Cf.* G. R. Husk, doctoral dissertation, University of Michigan, 1964.