

weaker complex than the monosulfide. Thus, at least with respect to iodine complexation, the disulfide is the better Lewis acid and the monosulfide the better Lewis base; this order causes no surprise since a similar behavioral difference exists between H_2O_2 and H_2O . However, in terms of charge transfer theory this may not be so readily explained. Since λ_{CT} and I_d are roughly equal for both the disulfide- and sulfide-iodine complexes and since the dipole moment of the disulfide is larger than that of the monosulfide (1.98 as compared with 1.47 d^{17}), the comparative instability of the disulfide-iodine complex must be sought in a comparative smallness of the DA overlap, $\int \varphi_A \varphi_D d\tau$, for this complex or in some steric factor. If we follow Hassel,¹⁸ the structure of the diethyl sulfide-iodine complex is that depicted in Fig. 3a and the DA overlap integral is $\int \varphi(3p_y S) \varphi(5d_{zy} I) d\tau$, with the three atoms, SI_2 , collinear. On the other hand, if we presume a structure for the diethyl disulfide complex with iodine similar to that in Fig. 3b the DA overlap integral is

$$\int \varphi(3p_x S^1 - 3p_y S^2) \varphi(5d_{(x+y)}(x+y)) d\tau$$

where the nomenclature used should be apparent from the figure. Since the acceptor orbital is the same in both cases, it is concluded that the magnitude of the DA integral is determined by the donor orbitals, at least for equal separation of donor and acceptor centers. Assuming reasonable values for the S—S distance and for the radial distance to the point of maximum amplitude of the 3p wavefunction of sulfur, it may be shown that the operative centers of maximum amplitude are $\sim 3/2$ to 2 times as far apart in the donor orbital of the disulfide as in the monosulfide. It would not be unreasonable on this basis to expect the DA overlap integral for the disulfide to be less than that for the monosulfide, and other things being equal to expect also a comparative instability of the complex

(17) C. C. Woodrow, M. Carmack and J. G. Miller, *J. Chem. Phys.*, **19**, 951 (1951).

(18) O. Hassel, *Proc. Chem. Soc.*, 250 (1957).

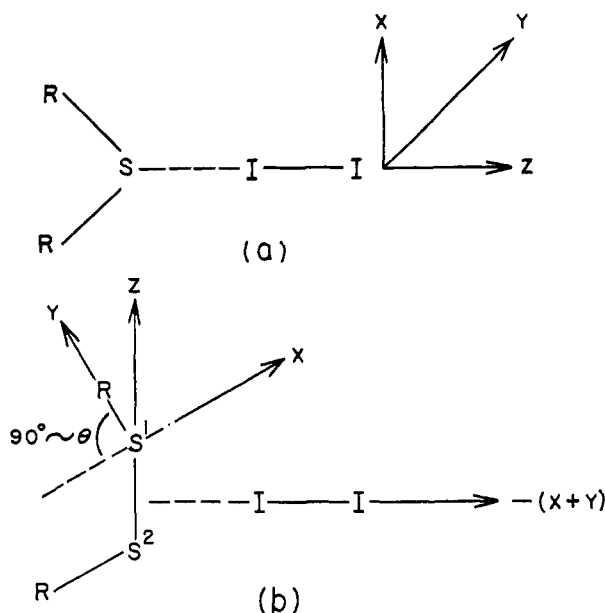


Fig. 3.—(a) The assumed structure of $(\text{C}_2\text{H}_5)_2\text{S}\cdot\text{I}_2$; it has been presumed that the structure of this complex is the same as that of diphenyl sulfide-iodine studied by Hassel¹⁸ by X-ray diffraction. (b) The assumed structure of $(\text{C}_2\text{H}_5)_2\text{S}_2\cdot\text{I}_2$. The axes here are defined independently of the definition in (a). The dihedral angle θ has been assumed equal to 90° and the superscripts on the sulfurs merely afford a method of labelling.

of the former with iodine. The fact that such is the case is presumed to favor structure b for the disulfide-iodine complex; it must be realized, however, that these latter conclusions can hardly be considered quantitative and should be accepted only with the proverbial grain of salt.

Acknowledgments.—The authors wish to express their gratitude to Professor J. G. Traynham of this department for much helpful discussion. They are also indebted to the agencies which granted this work their support.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA, LOS ANGELES 7, CALIFORNIA]

The Acid $\text{CF}_3\text{PO}_2\text{H}_2$, its Esters, Association and Structure¹

BY ANTON B. BURG AND JAMES E. GRIFFITHS

RECEIVED MAY 15, 1961

The phosphonous esters $\text{CF}_3\text{P}(\text{OCH}_3)_2$ (b.p. 89°) and $\text{CF}_3\text{PO}_2\text{C}_2\text{H}_4$ (m.p. -33° ; b.p. 113°) were made from CF_3PCl_2 and CH_3OH or $\text{C}_2\text{H}_4(\text{OH})_2$ respectively. Their infrared spectra agree with the formulas as written. The formation of the ring ester $\text{CF}_3\text{PO}_2\text{C}_2\text{H}_4$ was accompanied by considerable yields of less volatile products believed to be higher polymers of the same unit. Neither phosphonous ester showed any tendency for spontaneous rearrangement to the phosphinic ester form CF_3RPOOR , but the free acid $\text{CF}_3\text{PO}_2\text{H}_2$ gave infrared spectral evidence of existing almost wholly as the phosphinic acid dimer $(\text{CF}_3\text{HPOOH})_2$. For its vapor-phase dissociation to the monomer, $\Delta F^\circ = 16.00 - 0.0247T$ kcal. per mole of dimer, indicating $\Delta H^\circ = 8.00$ kcal. for each O—H—O bond. It is argued that the monomer is mostly CF_3HPOOH rather than $\text{CF}_3\text{P}(\text{OH})_2$.

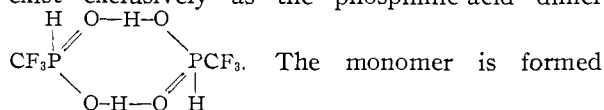
The phosphonous acid $\text{CF}_3\text{P}(\text{OH})_2$ has not been proved to exist as such; indeed, the corresponding

(1) This research was supported by the United States Air Force under a subcontract of Prime Contract AF 33(616)-6913, monitored by the Materials Laboratory, Wright Air Development Center, Wright-Patterson Air Force Base, Ohio.

sodium salt was shown to be the phosphinate $\text{Na}^+ \text{CF}_3\text{HPO}_2^-$, while the character of the free acid remained uncertain.² We now have made the dimethyl and dimethylene phosphonous esters $\text{CF}_3\text{P}-$

(2) F. W. Bennett, H. J. Emel us and R. N. Haszeldine, *J. Chem. Soc.*, 3598 (1954).

(OCH₃)₂ and CF₃PO₂C₂H₄, which do not spontaneously rearrange to the phosphinic ester forms; however, the corresponding free acid seems to exist exclusively as the phosphinic-acid dimer



The monomer is formed in the heated vapor, the equilibrium energetics of which strongly favor the CF₃HPOOH *versus* the CF₃P(OH)₂ form.

Such attachment of one H to P, in contrast to the favored attachment of H to O in (CF₃)₂POH,^{3,4} would mean that the phosphorus(III) atom has greater base strength when holding two O atoms and one CF₃ than when holding two CF₃ and one O. This difference would be surprising if one considered only the inductive effects in the P-C and P-O σ-bonding, for CF₃ and O have similar electronegativity and should similarly decrease the base action of the lone-pair electrons on P. However, the CF₃ group offers no way to compensate for this base-diminishing effect, whereas oxygen at least partially compensates by π-bonding, thereby returning electron density to phosphorus and enhancing the base action of its lone-pair electrons. There may also be more subtle effects related to differences in σ-bond hybridization. A different hybridization of phosphorus for P-C *versus* P-O σ-bonding would directly affect the shape of the orbital occupied by the phosphorus lone-pair electrons and so influence the bonding overlap with acidic atoms.⁵ Indeed, a very significant change of hybridization is likely to occur when oxygen forms π-bonds using P_{3d} orbitals: by all experience such π-bonds would widen the OPO bond angle. In any case, there is direct experimental evidence showing that P-O bonding greatly improves the base strength of phosphorus(III), for the (RO)₃P·BH₃ complexes are found to be extremely stable.⁶ This result would be most surprising if one considered only the inductive effect of the P-O σ-bonding upon base action by the phosphorus lone-pair electrons.

The Phosphonous Esters

Synthesis.—A mixture of 1.877 mmoles of CF₃-PCl₂^{7,8} and 3.959 mmoles of CH₃OH during 42 hr. at 25° gave 3.592 mmoles of HCl and 1.797 mmoles of CF₃P(OCH₃)₂, establishing the empirical formula of the latter. The 4% deficiency from the equation CF₃PCl₂ + 2CH₃OH → 2HCl + CF₃P(OCH₃)₂ was precisely explained by a slow secondary reaction, CF₃P(OCH₃)₂ + 2HCl → CF₃HPOOH + 2CH₃Cl, yielding 0.164 mmole of CH₃Cl. The ester was isolated by high-vacuum fractional condensation and exposure to P₄O₁₀ for removal of the last of the methanol.

(3) J. E. Griffiths and A. B. Burg, *J. Am. Chem. Soc.*, **82**, 1507 (1960).

(4) J. E. Griffiths and A. B. Burg, *Proc. Chem. Soc. (London)*, 12 (1961).

(5) This principle has been applied by J. H. Gibbs, *J. Phys. Chem.*, **59**, 844 (1955), to explain the dramatic increase of base strength when phosphine is methylated.

(6) T. Reetz, *J. Am. Chem. Soc.*, **82**, 5039 (1960).

(7) F. W. Bennett, H. J. Emeléus and R. N. Haszeldine, *J. Chem. Soc.*, 1565 (1953).

(8) W. Mahler and A. B. Burg, *J. Am. Chem. Soc.*, **80**, 6161 (1958).

Similarly, the dimethylene ester was made from 0.941 mmole of CF₃PCl₂ and 0.943 mmole of C₂H₄(OH)₂ (75% reaction in 45 min.; complete after 16 hr. at 25°), yielding 1.880 mmoles of HCl (99.9%). The ring-monomer CF₃PO₂C₂H₄ was isolated in 58% yield by passage through a high-vacuum trap at -35°, with condensation at -78°. The less volatile products separated into two fractions: a 15% yield trapped at -35° and a 27% yield of material which could be sublimed only by heating above room temperature. Both fractions evidently represented higher polymers of the CF₃P(OCH₃)₂C₂H₄O-unit rather than the rearranged CF₃P(OCH₃)₂C₂H₄O-unit,

for their basic hydrolysis rapidly and quantitatively converted all CF₃ groups to HCF₃, whereas hydrocarbon-P-CF₃ compounds give less HCF₃ even on long heating with strongly basic solutions.^{9,10} In sum, the demonstrable yield of CF₃P(OCH₃)₂C₂H₄-units was 0.930 mmole, or 98.8%, based upon the CF₃-PCl₂.

Formulas and Characterization.—The formulas CF₃P(OCH₃)₂ and CF₃PO₂C₂H₄ were confirmed by the vapor-phase mol. wts. (162.0 and 160.2 *vs.* calcd. 162.0 and 160.0) and by basic hydrolysis, rapidly giving one HCF₃ per mole, within the 1% experimental error. The m.p. of CF₃P(OCH₃)₂ could not be observed because it formed a glass at low temperatures; for CF₃PO₂C₂H₄, m.p. = -33.0°. The vapor tensions are shown with equations in Tables I and II. For CF₃P(OCH₃)₂, b.p. = 88.8° and Trouton constant = 22.7 cal./deg. mole. For CF₃PO₂C₂H₄, b.p. = 113° and Trouton constant = 21.3.

TABLE I

VAPOR TENSIONS OF CF₃P(OCH₃)₂

$$(\log P_{\text{mm.}} = 5.1731 + 1.75 \log T - 0.00355 T - 1985/T)$$

<i>t</i> (°C.)	-36.2	-22.8	0.00	16.0	24.9	32.8	44.4
<i>P</i> _{mm.} (obsd.)	1.29	3.56	15.83	38.85	61.1	89.1	148.9
<i>P</i> _{mm.} (calcd.)	1.29	3.57	15.86	38.82	61.1	88.9	149.0

TABLE II

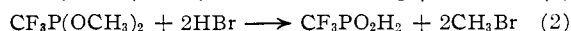
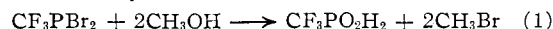
VAPOR TENSIONS OF CF₃PO₂C₂H₄

$$(P_{\text{mm.}} = 5.0948 + 1.75 \log T - 0.003702 T - 2051/T)$$

<i>t</i> (°C.)	-22.7	-4.7	0.00	10.7	14.4	20.6
<i>P</i> _{mm.} (obsd.)	1.5	5.1	6.9	12.9	15.9	22.1
<i>P</i> _{mm.} (calcd.)	1.5	5.1	6.9	12.9	15.8	22.1

The Free Acid

Synthesis.—The anhydrous acid having the empirical formula CF₃PO₂H₂ can be made by either of two closely related reactions



Both methods succeed because hydrogen bromide attacks the phosphonous ester far more rapidly than hydrogen chloride does. Thus in process (1) the first step surely is the formation of HBr and the ester, which then undergo reaction (2).

For method (1), 1.297 mmoles of CF₃PBr₂¹¹ and 2.800 mmoles of CH₃OH were condensed together at -196° in a weighed stop-cock tube attached to the high-vacuum manifold. A vigorous reaction occurred on warming to 25°. After 85 min. the

(9) R. N. Haszeldine and B. O. West, *J. Chem. Soc.*, 3880 (1957).

(10) L. R. Grant, Jr., Ph.D. Dissertation, University of Southern California Libraries, 1961, pp. 36, 60 and 79.

(11) A. B. Burg and J. E. Griffiths, *J. Am. Chem. Soc.*, **82**, 3514 (1960).

yield of CH_3Br (vapor tension 660.3 mm. at 0° ; known value, 660.0 mm.) indicated 75% completion of reaction (1), which became quantitative during 16 hr. The mixture was resolved by high-vacuum fractional condensation, with results demonstrating the empirical equation $1.295\text{CF}_3\text{PBr}_2 + 2.666\text{CH}_3\text{OH} \rightarrow 1.274\text{CF}_3\text{PO}_2\text{H}_2 + 2.543\text{CH}_3\text{Br}$. The desired acid appeared as a slightly volatile colorless liquid, having somewhat less tendency than $(\text{CF}_3)_2\text{POH}^3$ to be absorbed in the halocarbon stop-cock grease.

For method (2), 0.301 mmole of $\text{CF}_3\text{P}(\text{OCH}_3)_2$ and 0.602 mmole of HBr were held in a stop-cock tube for 24 hr. at 25° . The mixture was resolved by fractional condensation; empirical equation, $0.297\text{CF}_3\text{P}(\text{OCH}_3)_2 + 0.597\text{HBr} \rightarrow 0.297\text{CF}_3\text{PO}_2\text{H}_2 + 0.595\text{CH}_3\text{Br}$.

Formula and Volatility.—Both methods of synthesis quantitatively demonstrated the empirical formula $\text{CF}_3\text{PO}_2\text{H}_2$, which was checked further by the alkaline hydrolysis of a 40.4 mg. sample which had been made directly in a weighed stop-cock tube. With 20% aqueous NaOH during 30 min. at 25° it formed 0.301 mmole of HCF_3 (calcd. 0.301; mol. wt. 70.0, as calcd.). Molecular weight values approaching the value for $(\text{CF}_3\text{PO}_2\text{H}_2)_2$ were indicated by the vapor-phase equilibrium studies described in the next section. The purity of the substance was indicated by the consistent vapor-tension results shown with the equation in Table III; b.p. = 217° ; Trouton constant, 22.3 cal./deg. mole. Such a value of the Trouton constant would imply that the liquid and vapor phases have almost the same degree of association.

TABLE III

VAPOR TENSIONS OF $(\text{CF}_3\text{PO}_2\text{H}_2)_2$					
$(\log P_{\text{mm.}} = 3.9810 + 1.75 \log T - 0.0017706 T - 2419/T)$					
t ($^\circ\text{C.}$)	0.00	23.1	40.2	58.8	98.1
$P_{\text{mm.}}$ (obsd.)	0.08	0.41	1.17	3.33	20.18
$P_{\text{mm.}}$ (calcd.)	0.08	0.41	1.19	3.30	20.18

Vapor Phase Equilibria.—Pressure measurements were taken at six different temperatures, for a 0.2565 mmole sample of " $\text{CF}_3\text{PO}_2\text{H}_2$ " in an immersible tensimeter of known volume and with internal compensation for mercury vapor. The sample was made directly in the tensimeter by the ester-HBr method (equation 2), to avoid any loss due to transfer through the vacuum system. The results, shown in Table IV, are interpreted in terms

TABLE IV

VAPOR-PHASE EQUILIBRIA OF $(\text{CF}_3\text{PO}_2\text{H}_2)_2$							
t ($^\circ\text{C.}$)	$P_{\text{mm.}}$	Vol. of bulb (cc.)	Average mol. wt.	Per cent. dissociation	$K_{\text{atm.}}$ Obsd.	$K_{\text{atm.}}$ Calcd.	$\times 10^2$
134.1	15.81	224.4	246.0	9.0	0.68	0.66	
142.5	16.29	225.5	242.4	10.6	0.97	0.97	
150.1	16.85	225.6	238.6	12.3	1.36	1.38	
158.0	17.50	225.6	234.0	14.5	1.98	2.01	
165.3	18.12	225.6	229.8	16.6	2.70	2.67	
174.0	19.01	225.6	224.5	19.3	3.87	3.81	

of the dissociation of the dimer to monomer, undisturbed by any higher polymer such as the trimer. In fact, any appreciable amounts of trimer would have to be balanced by monomer, leading to a much higher Trouton constant. Also, the infrared spec-

trum for the saturated vapor at 98° (7 cm. cell) failed to show the 3600 cm.^{-1} O-H frequency which should appear for the monomer at partial pressures above the threshold of observation.

The equation correlating these results (for $K = P_{\text{m}}^2/P_{\text{d}}$) is $\log K_{\text{atm.}} = 5.400 - 3496/T$, or $\Delta F^0 = 16.00 - 0.0247T$ kcal. per mole of dimer. Thus the enthalpy of dimerization corresponds either to 8.00 kcal. for each of the two O-H—O bonds in the phosphinic acid dimer structure (see initial paragraph) or to 4.00 kcal. for each of the four O-H—O bonds in a phosphonous acid dimer structure wherein the four oxygen atoms would form a tetrahedron with four edges occupied by hydrogen. The 4.00 kcal. value would be lower than the normal 5–6 kcal. for O-H—O bonding with all oxygen atoms tricoördinate, whereas 8.00 kcal. per O-H—O bond involving only bicoördinate oxygen would be consistent with the 7.0–8.5 kcal. range of values found for carboxyl bridging in acetic acid.¹² In any case, the infrared spectrum argues against the phosphonous acid dimer but is altogether consistent with the phosphinic acid dimer structure.

The monomeric form of this phosphinic acid probably is not extensively converted to the phosphonous acid form, in this equilibrium system. If the monomer were mostly the phosphonous acid, the 16 kcal. ΔH value for the dissociation would include a subtracted $2\Delta H$ of conversion of the phosphinic acid to the phosphonous acid. Hence the actual ΔH per hydrogen bond would be considerably higher than the reasonable 8 kcal. value. Or, in the relatively improbable case that the two monomer forms be present in comparable proportions, the entropy of dissociation of the dimer into these two monomers would be higher than for dissociation into a single species. However, the actual ΔS value, 24.7 e.u., is 32% lower than the corresponding value (36^+ e.u.) for acetic acid.¹³ Indeed, it is not easy to find examples of similar dissociations for which ΔS is as small as in the present case. Thus there is little room for arguments favoring much conversion to the phosphonous acid.

Infrared Spectra

The Phosphonous Esters.—The infrared spectra of the esters $\text{CF}_3\text{P}(\text{OCH}_3)_2$ and $\text{CF}_3\text{PO}_2\text{C}_2\text{H}_4$ in the vapor phase were recorded by means of a Perkin-Elmer Infracord Spectrophotometer, using a 71 mm. cell with KBr windows. The patterns are compared with that for $\text{C}_6\text{H}_5\text{OPO}_2\text{C}_2\text{H}_4$ ¹⁴ in Fig. 1, and the probable assignments are shown together in Table V. The marked similarities of the main features lend confidence to these assignments, even though vibrational coupling effects introduce some uncertainties.

The most interesting feature shown by all three patterns is the set of three strong bands near 1020, 925 and 800 cm.^{-1} , corresponding to motions in the C—O—P—O—C unit. As might be expected, these are very closely similar for the two dimeth-

(12) A. W. Pross and F. van Zeggeren, *Spectrochim. Acta*, **16**, 563 (1960), and earlier references there cited.

(13) M. D. Taylor, *J. Am. Chem. Soc.*, **73**, 315 (1951); W. Weltner, *ibid.*, **77**, 3941 (1955).

(14) Sadtler's Standard Spectrum No. 9670, reproduced by permission.

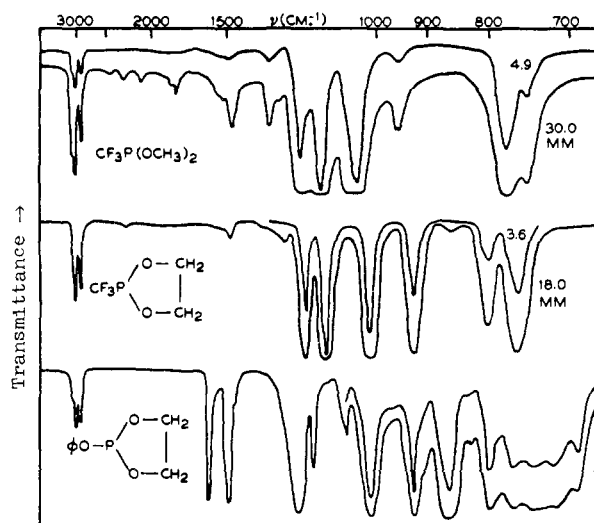


Fig. 1.—Comparison of infrared spectra of three esters.

ylene esters but somewhat deviant for $\text{CF}_3\text{P}(\text{OCH}_3)_2$. The assignment of the 800 cm^{-1} region to P-O stretching, and the 1020 cm^{-1} region to C-O stretching, is based upon our knowledge (yet to be published) of the spectra of $(\text{CF}_3)_2\text{POH}$, $(\text{CF}_3)_2\text{POD}$ and three of the esters $(\text{CF}_3)_2\text{POR}$. Then it becomes reasonable to assign the unique and strong band at 860 cm^{-1} to a stretching of the P- OC_6H_5 bond, while the common absorption bands in the 925 cm^{-1} region are attributed to a more complex motion involving all of the C-O-P-O-C bonds. The remaining assignments are more nearly routine, relative to the literature.¹⁵ The slightly high value for the CF_3 deformation band in the spectrum of $\text{CF}_3\text{PO}_2\text{C}_2\text{H}_4$ relative to other CF_3 -P compounds may be due to a contribution of the CH_2 rocking vibration to the band contour.

The Phosphinic Acid Dimer.—Nearly all of the expected main features of the spectrum of $(\text{CF}_3\text{HPOOH})_2$ are found in a record made by a Beckman IR7 grating spectrophotometer, using a 7 cm. cell fitted with KBr windows, at the normal instrument temperature of 40° (sample vapor at 1.1 mm.). A weak but fairly sharp absorption band centered at 795 cm^{-1} is attributed to a stretching of the P-O bond, although the band contour may be affected by the CF_3 deformation vibration. A strong doublet observed at 955 and 949 cm^{-1} with a weaker shoulder at 945 cm^{-1} probably is due to the bending of the P-H bond.¹⁶ The P=O stretching mode is assignable to a strong band at 1286 cm^{-1} , having on the mid-point of its slope a very sharp peak at 1307 cm^{-1} . The latter may well be a combination band, since one usually is observed in this region of the spectra of fluorocarbon phosphorus(III) compounds. Alternatively, it could be due to a splitting of the P=O stretching frequency as a result of molecular association. The C-F stretching vibrations are represented by a strong, sharp peak at

(15) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 2nd Ed., 1958, and references there cited.

(16) S. N. Nabi and N. Sheppard, *J. Chem. Soc.*, 3439 (1959); H. R. Linton and E. R. Nixon, *Spectrochim. Acta*, **15**, 146 (1959); H. C. Beachell and B. Katlafsky, *J. Chem. Phys.*, **27**, 182 (1957).

TABLE V

COMPARISON OF INFRARED SPECTRA OF THE ESTERS ^a			
Assignment	$\text{CF}_3\text{P}(\text{OCH}_3)_2$	$\text{CF}_3\text{PO}_2\text{C}_2\text{H}_4$	$\text{C}_6\text{H}_5\text{OPO}_2\text{C}_2\text{H}_4$
C-H stretch	3030 msh	3030 msh
	2930 s	3000 s	3000 m
	2880 m	2935 ms	2930 m
2×1208	2415 vw
2×1140	2280 vw	2260 vw
$2 \times 1040?$	2090 vw
Combination?	1800 vw
C-C stretch in C_6H_5	1600 s
C-H deformation in CH_3 and CH_2 groups	1520 w
	1475 mw	1480 vw	1490 s
Combinations?	1455 vw
	1315 mw
O- C_6H_5 stretch	1280 vw	1255 vw
	1215 s
C-F stretch	1208 vs	1192 vs
	1140 vs	1130 vs
Uncertain	1163 m
	1072 mw
C-O-P-O-C stretch	1040 vs	1022 vs	1015 s
C-O-P-O-C complex	953 m	928 m	922 s
P- OC_6H_5 stretch	860 s
	828 w
CO-P-OC stretch	775 s	805 ms	803 ms
	767 m
Aromatic C-H out-of-plane bending	720 m
	715 m
	690 m
CF_3 deformation	750 w	764 s

^a Frequencies are given in cm^{-1} . sh = shoulder; v = very; s = strong; m = medium; w = weak.

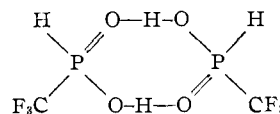
1228 cm^{-1} and a very strong, nearly merged doublet at 1166 and 1142 cm^{-1} . P-H stretching appears quite clearly as a medium-weak but very sharp band at $2425 \pm 2\text{ cm}^{-1}$, surrounded by weaker satellites at $2610 \pm 30\text{ cm}^{-1}$ (2×1286 , raised to 2610 by Fermi resonance with the 2425 cm^{-1} band), at $2275 \pm 15\text{ cm}^{-1}$ (2×1142) and at $2120 \pm 15\text{ cm}^{-1}$ ($2 \times 1071, q.v.$). We have noticed similar satellites in the spectra of two other CF_3 -P-H compounds.

The O-H—O stretching region is represented by four medium-weak peaks at 2988 , 2967 , 2930 and 2857 cm^{-1} , all measured with a probable error of 1 cm^{-1} . Since the 40° spectrum failed to show the slightest trace of the 3600 cm^{-1} band which is to be expected for free O-H stretching in monomeric CF_3HPOOH or $\text{CF}_3\text{P}(\text{OH})_2$, the spectrum was recorded also at higher temperatures, with the 7 cm. cell enclosed in an insulating box having NaCl windows. Thus the temperature of the cell could be controlled by passing hot air from a heater-blower through the box, without affecting the 40° controlled cell-chamber of the IR7 instrument.

With this arrangement, the 2988 and 2967 cm^{-1} peaks were merging at 70° , and at 95° they appeared as one broader peak centered at $2977 \pm 3\text{ cm}^{-1}$. The 3600 cm^{-1} band, however, still was not observed above the background, even at 98° (saturated vapor), where it is calculated that the monomer would have a partial pressure of 0.12 mm. if the data of Table IV are interpreted on the basis of a purely monomer-dimer equilibrium. By

any interpretation implying much more monomer, the usually very strong 3600 cm.^{-1} band surely would be expected to appear.

A distinct band of medium intensity at 1071 cm.^{-1} is attributed to an O-H bending by analogy with the assignments which we have made for the $(\text{CF}_3)_2\text{POH}$ molecule and further confirmed by means of the $(\text{CF}_3)_2\text{POD}$ spectrum. An equally intense band at 999 cm.^{-1} is not readily identifiable but may be due to complex motion within the cyclic dimer framework



The presence of bands corresponding to P-H and P=O stretching vibrations, as well as the O-H—O vibrations in the expected regions, are all strongly in favor of the phosphinic acid dimer structure and against the quadruply H-bridged $\text{CF}_3\text{P}(\text{OH})_2$ dimer. Thus the spectrum confirms the indications from the energetics of the vapor-phase equilibria.

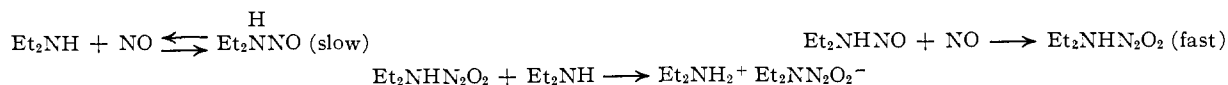
[CONTRIBUTION FROM THE WM. A. NOYES LABORATORY, CHEMISTRY DEPARTMENT, UNIVERSITY OF ILLINOIS, URBANA, ILLINOIS]

A Mechanism for the Reaction of Diethylamine with Nitric Oxide

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Kinetic data are presented in support of a mechanism for the reaction of diethylamine with nitric oxide. The mechanism shown for formation of the product, $\text{Et}_2\text{NH}_2^+\text{Et}_2\text{NN}_2\text{O}_2^-$, is consistent with the observed kinetic data

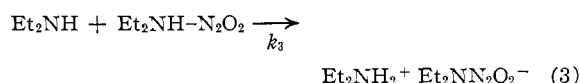
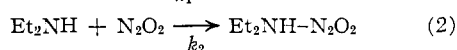
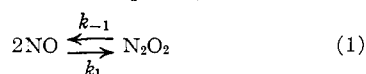


An activation energy of about 12 kcal. is obtained for the reaction.

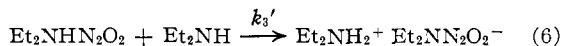
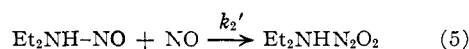
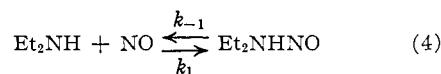
Introduction

In an earlier article² it was shown that nitric oxide reacts with diethylamine to produce the compound $\text{Et}_2\text{NH}_2^+\text{Et}_2\text{NN}_2\text{O}_2^-$. Structural evidence was presented. By extending³ this reaction to a whole series of amines it was demonstrated that this is a general reaction type for nitrogen(II) oxide.

Two possible mechanisms for this reaction were considered. One involves the attack of base on the nitric oxide dimer. Although detectable quantities of N_2O_2 are not observed under reaction conditions, a kinetically important amount may exist resulting in the reaction path (I)



A second possible mechanism (II) is outlined



A kinetic study was undertaken to provide information concerning the reaction mechanism.

(1) Abstracted in part from the Ph.D. Thesis of R. O. Ragsdale, University of Illinois, Urbana, Ill. (1960).

(2) R. S. Drago and F. E. Paulik, *J. Am. Chem. Soc.*, **82**, 96 (1960).

(3) R. S. Drago and B. R. Karstetter, *ibid.*, **83**, 1819 (1961).

Experimental

Purification of Reagents. Diethylamine.—Purification of diethylamine was necessary to prevent erratic results. Reagent grade diethylamine was refluxed 2 to 3 hr. over barium oxide. The middle fraction obtained upon distillation was stored in a desiccator and employed in these experiments.

Nitric Oxide.—Nitric oxide was purified by bubbling through 10 *M* KOH and dried by passing over solid NaOH pellets.

Methanol.—Reagent grade methanol was employed.

Apparatus.—A Cary Recording Spectrophotometer Model 14 was used for recording the ultraviolet spectra. Matched 1.00 cm. quartz cells with ground glass stoppers were employed. Polyethylene film was fastened over the stopper with a rubber band to prevent loss of nitric oxide to the atmosphere. No change was observed in the spectra of nitric oxide solutions over a period of 24 hr. The base line was checked every 30 minutes during a kinetic run.

Extinction Coefficient Determinations.—Nitric oxide was absorbed into a methanol solution from a gas buret. The experiment was conducted in a closed system and the volume of nitric oxide absorbed was measured. In three different experiments a value of ϵ_{NO} equal to 52 ± 1 (l. mole⁻¹ cm.⁻¹) was obtained at $346\text{ m}\mu$. This frequency was selected to follow the appearance of product. It was also demonstrated that nitric oxide obeys Beer's law in the concentration range employed. The extinction coefficient of nitric oxide was found to increase upon the addition of amine. The value of ϵ_{NO} in the presence of amine was determined by extrapolating back to zero time, readings obtained for the first 30 minutes after the addition of amine to an NO solution. A value of $\epsilon_{\text{NO}} = 54 \pm 1$ l. mole⁻¹ cm.⁻¹ was obtained.

The product of the reaction $\text{Et}_2\text{NH}_2^+ \text{Et}_2\text{NN}_2\text{O}_2^-$ also absorbs in the $350\text{ m}\mu$ region of the spectra (see curve 4 of 1). The molar absorptivity of the product, ϵ_p , cannot be accurately measured directly. There was probably decomposition of some of the product in the course of preparing the solution as evidenced by noticeable loss of NO from more concentrated solutions. This difficulty in measuring ϵ_p can be circumvented by taking advantage of the isosbestic point for the product and nitric oxide at $350\text{ m}\mu$ (Fig. 1). At this point ϵ_{NO} equals $1/2\epsilon_p$ and direct measurement of ϵ_{NO} at this wave length in amine solution enables calculation of ϵ_p . At $350\text{ m}\mu$ a value of ϵ_p equal to 159 ± 1 is obtained. The