while the correlation is much better for the *m*- and *p*-fluorines. Now in the tri- and tetrasubstituted benzenes studied by us, all the fluorines whose shifts have been measured are adjacent to at least one proton. It may be that there is sufficient "complexing" of the solvent around the relatively electron-deficient protons in these molecules to produce large van der Waals shifts which "swamp" the "reaction field" contribution to the shifts. It must also be noted that in some meta- and para-substituted fluorobenzenes[19,42] good agreement with the reaction field term is found, even though there are four "free" proton positions. In this case, however, the reference was monofluorobenzene, so perhaps the effects of "complexing" at the protons are thereby effectively eliminated. This would not be the case for the fully fluorinated C_6F_6.

Acknowledgment. We are grateful to Professor Kenneth L. Servis for helpful discussion and the use of the sample of 1-methyl-4,7-difluorophenanthrene. We thank Professor Frank B. Mallory and Dr. Clelia S. Mallory for synthesizing the 1,5-difluoro- and 1,8-difluoronaphthalene.

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Recoil Tritium Reactions with Cyclohexene Including the Pressure Dependence of the Unimolecular Decomposition[1,2]

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Abstract: The reaction of recoil tritium with cyclohexene was studied in the liquid phase and at pressures from 9 to 1400 Torr in the gas phase. Products observed in the work were HT, ethene-*t*, 1,3-butadiene-*t*, *n*-hexenes-*t*, methylcyclohexane-*t*, propene-*t*, cyclohexane-*t*, cyclohexene-*t*, and tritiated polymers. Comparison of the recoil tritium–cyclohexene system with known parameters from earlier kinetic studies of the unimolecular decomposition of cyclohexene to ethene plus 1,3-butadiene shows an average excitation energy of 5 eV/molecule for the gas-phase species undergoing this decomposition and 8–12 eV/molecule for the same decomposition in the liquid phase. The observed ratio of cyclohexane-*t*/*n*-hexene-*t* led to an average rate constant of 1.0×10^8 sec^{-1} for decomposition of cyclohexyl-*t* radicals in this system.

Butler and Kistiakowsky[4] have shown the equivalence of different ground electronic state vibrational excitation modes in determining the fate of unimolecular decompositions which proceed by way of an internally equilibrated intermediate. Also similar products have been observed in pyrolysis,[5] shock-tube,[6] and photochemical studies of cyclohexene[7] decomposition. The present work extends these studies to the use of recoil tritium as an excitation source to study the pressure dependence of the unimolecular decomposition of cyclohexene. In this system, the initial locus of excitation is that C–T bond at which tritium has undergone direct substitution for H on the cyclohexene molecule.

Experimental Section

In this work it was necessary to study the cyclohexene decomposition reaction over a wide range of pressures. Samples with vapor pressures above the cyclohexene room-temperature vapor pressure were prepared with the sample ampoule temperature in the range 25–135°. This was done using a specially constructed vacuum system within an oven as was previously described.[8] The oven temperature was the parameter varied to reach the desired cyclohexene vapor pressure. The samples in which the cyclohexene pressure was below 7.0 cm were filled by sequential addition of ^{3}He, moderator gases, and cyclohexene on a vacuum line. LiF (natural abundance ^{6}Li, Riedel-de-Haen, West Germany) was used as the tritium source for liquid-phase studies. Pyrex 1720 sample ampoules were used for both gas and liquid phase studies. All ampoules were "flamed out" *in vacuo* before use.

Neutron irradiations of samples were performed at the Missouri University Research Reactor. The nominal flux was 1.4×10^{12} n cm^{-2} sec^{-1} and irradiations were typically 3–5 min. The γ intensity was $4.2 \pm 0.4 \times 10^7$ rads/hr. When irradiating at a lower flux, the irradiation time was longer so that a similar integral flux was seen by all samples. The external γ radiation and the internal radiation due to the recoil tritium and recoil proton gave radiation damage less than 1%.[8]

The sample holder for the irradiations was an aluminum vessel which contained an aluminum block with bored holes to hold the ampoules. For the samples in which the cyclohexene vapor pressure exceeded 7.0 cm, the sample ampoules were placed in the block holes and heated to the temperature necessary to avoid any condensation before or during irradiation. The block and samples were then placed in the irradiation vessel and its lid was fastened using a polyethylene O-ring to ensure that the vessel was water tight during irradiation. Since the rate of cooling with respect to time was known, it was possible to determine an average temperature and pressure which existed during irradiation.

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(1) Presented in part before the 158th National Meeting of the American Chemical Society, New York, N. Y., 1969.

(2) A portion of the material was submitted by R. W. W. in partial fulfillment of the requirements for the Ph.D. degree, University of Missouri.

(3) (a) American Oil Co.; (b) Washington State University.

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Table I. Product Yields Relative to Cyclohexene-*t* = 100 (Gas Pressures in Torr × 10^{-1})[c]

Cyclohexene	^{3}He	^{4}He or Xe	Total	HT	Ethene-*t* + 1,3-butadiene-*t*	*n*-Hexenes-*t*	Cyclohexane-*t*	Methylcyclohexane-*t*	Polymer-*t* Light	Polymer-*t* Heavy
4,4	1.5	5.0	10.9	275	42	4.8	31	4.2	30	75
2.4	1.4	11.2	15.0	273	36	4.6	41	10	28	107
2.4	1.4	11.2	15.0	294	43	4.1	44	12	24	99
2.5	1.5	24.9	28.9	273	32	2.7	62	17	38	122
3.4	1.1	78.3	82.0	308	28	4.7	196	15	Lost	107
3.4	1.1	78.3	82.0	309	30	5.3	195	11	53	138
2.9	1.5	14.6[b]	19.0	209	34	5.8	37	6	19	25
4.5	1.5	20.6[b]	26.6	233	33	6.7	41	*a*	16	43
5.0	1.8	36.4[b]	43.2	204	28	5.9	46	5	19	95

[a] Not resolved from cyclohexene owing to variation in procedure. [b] Xenon. [c] Reference 12.

Table II. Unmoderated Sample Product Yields Relative to Cyclohexene-*t* = 100

Av pressure during irradiation, Torr × 10^{-1} Cyclohexene	^{3}He	Total	Temp, °C	HT	Ethene-*t* + 1,3-butadiene-*t*	*n*-Hexene-*t*	Cyclohexane-*t*	Methylcyclohexane-*t*	Propene-*t*	Polymer-*t* Light	Polymer-*t* Heavy
0.9	1.1	2.0	25	221	55					104	101
2.6	1.4	4.0	25	237	55	10.0	21.5	6.0	1.6	61	20
15.5	0.8	16.3	85	272	38.6	6.2	33.5		1.9	172	35
18.0	1.3	19.3	86	250	36.3					50	11
37.9	0.7	38.6	85	339	32.5	8.5	57.0		0.5	27	8
41.4	3.6	45.0	81	231	30.1	7.0	53.0		1.3	16	15
60.2	1.3	61.5	103	372	19.0	5.9	41.0	1.0	0.6	56	11
73.8	1.0	74.8	103	316	36.6	7.8	93.0	2.4	0.2	40	7
120.0	1.3	121.3	103	240	27.2	6.0	75.2		0.3	18	5
141.0	1.4	142.4	135	201	23.4	1.0	22.6			24	6
5.3 ± 0.4 mg of LiF			25	269	10.6	8.0	52.0	0.5	1.5	20	12
			25	274	8.2	5.6	44.0		0.2	18	6
			25	294	7.1	7.8	39.0	1.1	1.5	42	18

After allowing a proper time interval for the decay of ^{27}Al in the irradiation vessel, the samples were analyzed by the radiogas chromatography[9] and liquid scintillation techniques[10] previously described.

Discussion

HT formation in recoil tritium–hydrocarbon systems has been postulated as resulting from both atom–molecule[11] and ion–molecule[12,13] (IM) reactions. In earlier recoil tritium work only tritium atom–molecule abstraction reactions were proposed for HT formation in pure hydrocarbon systems. However, as seen in the data of Tables I and II, the HT yields in an unmoderated system are in better agreement with helium-moderated samples (wherein IM contributions to HT formation have been proposed) than with xenon-moderated samples. IM contributions to HT formation in the pure hydrocarbon system are not likely since the yields of other products (polymer-*t* and methylcyclohexane-*t*) postulated as having been formed by IM pathways[12] are not high as they are in the helium-moderated samples. A more likely explanation is that the HT yield was a function of the temperature of the system. In this work on unmoderated samples, a higher pressure also meant a higher temperature. This would be in keeping with the observation that HT yields do increase with temperature in other systems[14] and the lack of a clear pressure dependence for HT formation in moderated samples.[12] A higher reactivity integral value for HT formation by tritium abstraction at low energies could account for this.[14]

Photolysis studies[7] in which cyclo-C_6H_{10}* is formed showed that it is not likely that an appreciable amount of HT was formed from the decomposition of cyclo-C_6H_9T.

The direct substitution of T for H in cyclohexene has been suggested as occurring by a hot as opposed to a thermal mechanism.[15] The present and previous work confirm this through correlating observed behavior with the behavior expected in accordance with the Estrup–Wolfgang kinetic theory of hot reactions. As expected for a hot process, the ratio (cyclohexene-*t*)/(total observed tritium) decreased as the mole fraction of moderating gas in the system increased. Since those tritium species undergoing the T for H substitution give cyclohexene-*t* molecules with a variety of excitation energies, it follows that a number of reaction pathways may ultimately be possible for the tritiated cyclohexene molecule.

Doepker and Ausloos[7] have shown that for the unimolecular decomposition of cyclohexene, either electronic excitation or vibrational excitation may lead to certain of the same products. For the products ethene and 1,3-butadiene this may be explained by considering the C–C bond energies (kcal/mol) of cyclohexene and

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(9) K. I. Mahan, R. W. Weeks, Jr., D. C. Fee, and J. K. Garland, *Anal. Lett.*, 1, 933 (1968).

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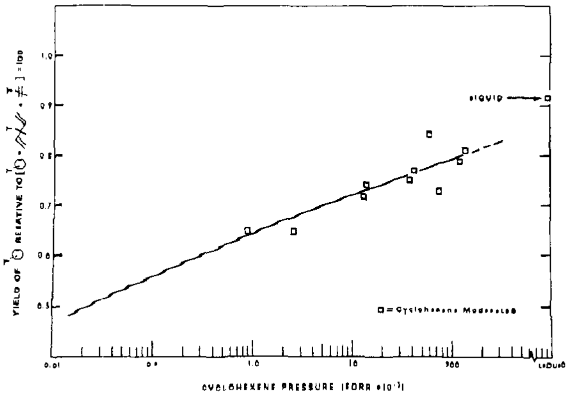
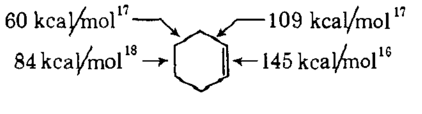


Figure 1. Unimolecular decomposition product yield as a function of pressure.

considering cleavage of an internally excited cyclohexene molecule at the weakest C–C bonds.



The substitution of T for H is roughly independent of aliphatic C–H bond strength[19] and would allow somewhat comparable C–T loci of excitation at positions 3, 4, 5, or 6. From these different initial loci of excitation would come an internally equilibrated intermediate which would cleave at the weakest C–C bonds to yield the observed products, ethene plus 1,3-butadiene.

As mentioned earlier, cyclohexene is known to undergo unimolecular decomposition to ethene plus 1,3-butadiene by pathways which involve either vibrational excitation[5,6] or electronic excitation.[7] In this work it is not possible to distinguish between these pathways and the various amounts of excitation a species might have along either pathway. Neither pathway can be ignored in view of the existence of both atomic[11] and/or ionic or electronically excited[12] tritium in some recoil systems.

Electronically excited cyclohexene-*t* might be formed either by conversion of translational to electronic energy[20] or by the direct substitution reaction of ionic or electronically excited tritium. A semilocalized molecular orbital approach[21] has been used to show the involvement of electronic excitation in the unimolecular decomposition of cyclohexene. Also, the possibility for the involvement of predissociation exists, as has been shown by translationally hot species inducing this mechanism.[22] Recoil tritium may produce such pathways here. The formation of ionic cyclohexene intermediates could lead to the general fragmentation pathway proposed by Miyazaki, *et al.*[23]

Additionally, for those cyclohexene molecules which become electronically excited, the time necessary for distribution of the electronic excitation from the initial excitation loci to the remainder of the molecule will be of the order of 10^{-14}–10^{-15} sec.[24] These excited species could then decompose within the period of a single vibration. This is clearly not the fate of all cyclohexene-*t* molecules, because some are not decomposed even at low pressures in the gas phase.

That vibrational excitation can cause the unimolecular decomposition of cyclohexene to ethylene plus 1,3-butadiene is well established.[5,6] In the present investigation, the gas-phase yield of unimolecular decomposition products as a function of pressure shows that a wide range of excitation energies causes this decomposition. The lower limit energy of those species undergoing decomposition would be the threshold energy. Using Slater's[25] approach, this would be a minimum excitation of 66.2 kcal mol^{-1}. As will be shown later, the median excitation energy in the gas phase is 5 eV, and certainly some species are excited to a greater value than this.

For vibrational excitation with an internally equilibrated intermediate, it is possible to employ the RRK formulation to determine the average amount of excitation energy leading to decomposition in this system. From Figure 1 and Table II it may be seen that the half pressure for this decomposition is approximately 0.2 Torr. The average time between collisions of cyclohexene molecules at this pressure is

$$(0.02Z_{11})^{-1} = 1/(4.6 \times 10^5) = 2.2 \times 10^{-6} \text{ sec}$$

From this, and the strong collision assumption, it is possible to determine a lower[26] limit of the apparent first-order rate constant as $k = 0.693/(2.2 \times 10^{-6}\ \text{sec}) = 3.1 \times 10^5\ \text{sec}^{-1}$.[27] It must be realized that this value is really a composite of the rate constants for all amounts of excitation and represents a median of excitation. By employing the RRK formula $k_{\text{decomp}} = A[(E - E_0)/E]^{s-1}$ and parameters used in previous work[5,6,28] it was possible to estimate the average gas-phase excitation energy as 5 eV. This is in good agreement with, but slightly lower than, the excitation energy per degree of freedom observed in the recoil-tritium-induced unimolecular decomposition of cyclobutane.[29] Employing the same parameters in the liquid phase and estimating an average specific rate constant of 10^{10} to 10^{12} sec^{-1} (of the order of magnitude for liquid-phase vibrational relaxation in polyatomics),[30] a value of 8–12 eV per molecule is obtained for the average excitation energy.

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(17) R. T. Morrison and R. N. Boyd, "Organic Chemistry," Allyn and Bacon, Boston, Mass., 1959, p 39.

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(26) T. A. Whatley and D. F. Swinehart, *J. Amer. Chem. Soc.*, **91**, 7617 (1969).

(27) Some molecules would decompose before collision and the subsequent deactivation. The average lifetime of those species undergoing decomposition would be less than 2.2×10^{-6} sec and the actual rate constant larger than $3.1 \times 10^5\ \text{sec}^{-1}$. Calculations by Dr. A. P. Yu (American Oil Co., Whiting, Ind.) using the IBM 360 computer and the Whatley–Swinehart[26] average lifetime of those species undergoing decomposition have shown that a more accurate value of k_{decomp} would be $6.2 \times 10^5\ \text{sec}^{-1}$.

(28) N = number of atoms in molecule, $A = 10^{15.2}$, $E_0 = 66.2$ kcal mol^{-1}, s = number of effective oscillators = $^2/_3(3N - 6) = 28$.

(29) E. K. C. Lee and F. S. Rowland, *J. Amer. Chem. Soc.*, **85**, 897 (1963).

(30) R. G. Gordon, W. Klemperer, and J. I. Steinfeld, *Annu. Rev. Phys. Chem.*, **19**, 215 (1968).

The fact that the yield of cyclohexane-*t* increased as the ratio (moderator)/(cyclohexene) increased[12] was taken as evidence for the formation of cyclohexane-*t* through a thermal pathway in moderated samples. Particularly, at a high degree of moderation the reactive tritium species will reach a lower average energy before engaging in a reactive encounter. It should be kept in mind that there will still be an energy spread for those tritium atoms undergoing addition to the double bond.

The most likely reaction pathway for the more highly moderated low-energy species would be T addition to the double bond to form the cyclohexyl-*t* radical. This radical could then undergo proton abstraction to form the cyclohexane-*t*. Further support for this is seen in the data for unmoderated samples. There was a general trend for a gradual increase in cyclohexane-*t* as the pressure of the system increased. Because in these systems the temperature increased as the pressure increased, the $^3/_2kT$ energy of the tritium and the energy of the resultant cyclohexyl-*t* radicals would have been larger at higher temperatures. It was possible that a higher proportion of the low-energy tritium would then have had the minimum energy necessary for addition to the double bond of cyclohexene. Also, at higher pressures, the relative number of cyclohexyl-*t* radicals decomposing and the recoil T loss to the walls would have been less.

In addition to proton abstraction the cyclohexyl-*t* radical may undergo C–C bond cleavage (at the position β to the radical carbon).[31] This particular pathway would lead to the formation of a hexenyl-*t* radical. This could then react by proton abstraction to form *n*-hexene-*t*. By assuming that the cyclohexane-*t* and hexene-*t* yields were related to the cyclohexyl-*t* and hexenyl-*t* radicals, respectively, it was possible to determine the S/D (stabilization/dissociation) ratio as a function of the total pressure and the (moderating gas)/(cyclohexene) ratio.

In addition to being a function of the system's pressure (as shown by the general trend of increasing cyclohexane with increasing pressure in unmoderated samples, Figure 2), for helium-moderated samples the S/D ratio was also a function of the mole ratio of moderator gas to cyclohexene (MG/HC) in the sample.[12] At high MG/HC mole ratios, tritium undergoing addition to the double bond would be moderated to a lower average energy before the addition. The resultant cyclohexyl-*t* radical would be less excited and less subject to decomposition. The fact that the $(S/D)^{-1}$ ratio did not vary linearly as $1/P$ showed a spread in the energy with which the cyclohexyl-*t* radical was formed.

The pressure dependency of the scission *vs.* stabilization reactions would be such that at high pressures more rapid deexcitation of the cyclohexyl-*t* radical would allow a higher S/D ratio. This general trend was observed for the unmoderated samples.

Knowing the S/D ratio at a given pressure allowed calculation of the apparent rate constant for cleavage of the cyclohexyl-*t* radical. This assumed that the dominant ultimate chemical fate of the hexenyl-*t* and cyclohexyl-*t* radicals was the formation of *n*-hexene-*t* and cyclohexane-*t*, respectively. At a pressure of 2.6 cm in the unmoderated samples the S/D ratio was 1.0, as determined by graphical extrapolation on a plot of S/D *vs.* log P_{total}. Employing the formula[32] $k_a = \omega(\text{S/D})^{-1}$ (ω is the collision number and k is the apparent rate constant) and the strong collision assumption, the apparent rate constant for decomposition of the cyclohexyl-*t* radical is 6.3×10^7 sec^{-1}. Based on the assumptions of Whatley and Swinehart,[26] a more accurate value of the average rate constant at this pressure would be greater than this by perhaps a factor of 2,[26] *i.e.*, 1×10^8 sec^{-1}. This higher value resulted from the use of the average, rather than the maximum lifetime of those species which reacted, *i.e.*, underwent C–C bond scission, and also the deletion of lifetimes of activated radicals deactivated by collision. When compared to literature values of the decomposition of alkyl radicals,[33–35] the present value is somewhat higher.

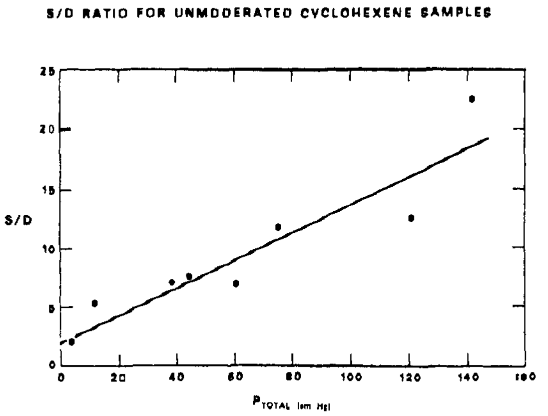

Figure 2. The stabilization/dissociation (S/D) ratio for the cyclohexyl-*t* radical as a function of the total pressure of the system.

The fact that the S/D ratio drops to a relatively low value in the liquid phase in anomalous. One possible explanation is that excitation in modes other than vibrational may exist. Ionic pathways for decomposition fall into two categories, the more rapid of which is pressure independent.[23] The possibility of predissociation or exciton transfer likewise cannot be ruled out. Either of these mechanisms would account for the lack of deactivation and hence the existence of unimolecular decomposition that is observed in the liquid phase.

The fact that the gas-phase S/D ratio did not equal zero at zero pressure may have been either real or virtual. If real, it may be explained as follows. Among the possible deviations from the principal cyclohexyl radical products, *n*-hexene and cyclohexane, are possible cyclohexyl addition to cyclohexene, hexenyl radical isomerization to the cyclopentylmethyl radical,[36] and cyclohexyl radical decomposition or cyclohexane unimolecular decomposition to form ethene plus 1,3-butadiene.[7] The higher temperatures required for the higher pressure studies may lead to a faster decomposition of cyclohexane. That this contribution, if present, was small, may be seen in Figure 2 where the high-pressure data points are within the limits of experimental error on the plot in which this reaction is not

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(32) C. W. Larson and B. S. Rabinovitch, *J. Chem. Phys.*, **51**, 2293 (1969).

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considered. Other reaction pathways are of minimal importance and are neglected in this zero-order treatment of the experimental data.

The amount of propene-*t* was small in both moderated and unmoderated samples.[12] It was possible for fragmentation to yield a C_3 unit in a manner akin to that observed in certain pyrolysis studies.[37] The small yield of this product did not allow the discerning of yield differences in the various systems.

Polymeric materials were arbitrarily defined as those tritiated species C_8-*t* or greater which were not eluted through the column during the forward-flow sequence. The higher yields in helium-moderated samples were interpreted as resulting from ion–molecule contributions in this environment. Possible reaction pathways have been mentioned previously.[11] It is interesting to note that in unmoderated samples there is a trend for light polymer-*t* to exceed heavy polymer-*t* several-fold. The opposite is true in moderated samples.

The yield of methylcyclohexane appears to be higher in moderated samples. There is an obvious increase in the yield of this product with increasing mole fraction in helium-moderated samples, and this may be interpreted as being due to IM contributions. One possible reaction pathway for this product would be tritium attack on a given carbon atom, with the subsequent cleavage of contiguous C–C bonds to form a CH_2T radical or ion. Radical formation by addition of this species to the cyclohexene double bond where followed by hydrogen abstraction would give methylcyclohexane.

Conclusions

As expected for recoil chemistry, a wide variety of products has been observed in this work. A median excitation energy for the unimolecular decompositions of cyclohexene-*t* has been determined to be 5 eV for the gas-phase studies. The liquid-phase studies gave a median excitation energy of 8 eV. These calculations are based on the premise that the formation of ethene-*t* and 1,3-butadiene-*t* results primarily from the unimolecular decomposition of an initially excited cyclohexene-*t* molecule. It is possible that other minor pathways also contribute to these products.

The S/D ratio of decomposition of the cyclohexyl-*t* radical was shown to be a function of the mole ratio of moderator in moderated samples. In unmoderated samples a pressure dependence of the ratio was observed. The fact that $(S/D)^{-1}$ was not a linear function of P^{-1} in either moderated or unmoderated samples showed that the postulated cyclohexyl-*t* precursor had a wide variety of excitation energies. The rate constant for the decomposition of the cyclohexyl-*t* radical was determined to be 1.0×10^8 sec^{-1}.

Acknowledgments. Fellowship support from the Gulf Oil Corp., Monsanto Co., and the donors of the Petroleum Research Fund is gratefully acknowledged by R. W. W., Jr. The calculations by Dr. A. P. Yu are appreciated.

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Synthesis and Characterization of Bis(trifluoromethyl)thiophosphoryl-μ-thio-bis(trifluoromethyl)phosphine and Di(bis(trifluoromethyl)thiophosphoryl) Disulfide

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Contribution from the Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada. *Received May 14, 1970*

Abstract: Bis(trifluoromethyl)iodophosphine sulfide reacts with limited quantities of mercury to give the diphosphorus compound $(CF_3)_2P(S)$–S–$P(CF_3)_2$ in which the phosphorus atoms are bridged by a sulfur atom. This same compound is better synthesized from the reaction of bis(trifluoromethyl)dithiophosphinic acid with either dimethylaminobis(trifluoromethyl)phosphine or with chlorobis(trifluoromethyl)phosphine. The mixed-valence compound is stable to air or sulfur oxidation but reacts with hydrogen halides, halogens, and mercury. Hydrolysis by water and alkaline solutions gave 1 and 3 mol of CF_3H, respectively, per mole of compound. The diphosphine tetrasulfide, $(CF_3)_2P(S)SSP(S)(CF_3)_2$, was best prepared by bromination of salts of bis(trifluoromethyl)dithiophosphinic acid. The tetrasulfide also reacted with mercury, halogens, hydrogen halides, and hydrogen sulfide, but not with oxygen or sulfur. Alkaline hydrolysis gave 2 mol of CF_3H per mole of compound, while neutral water yielded no CF_3H. A simpler synthesis of $(CF_3)_2P(S)SH$ is also described.

The recent syntheses of bis(trifluoromethyl)dithiophosphinic acid[1,2] and related trifluoromethylphosphine sulfides has led to an extensive study of the chemistry of this system. We wish to report herein details of the synthesis and properties of the mixed-valence compound[3] $(CF_3)_2P(S)$–S–$P(CF_3)_2$ and the related tetrasulfur–diphosphorus compound $[(CF_3)_2P(S)]_2S_2$. The possible existence of the mixed-valence compound

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[1] R. C. Dobbie, L. F. Doty, and R. G. Cavell, *J. Amer. Chem. Soc.*, **90**, 2015 (1968).

[2] K. Gosling and A. B. Burg, *ibid.*, 90, 2011 (1968).

[3] For a preliminary communication on the mixed-valence compound, see R. G. Cavell, T. L. Charlton, and A. A. Pinkerton, *Chem. Commun.*, 424 (1969).