

as was observed with the tank nitrogen. This observation eliminated the possibility that the 42^+ might be due to $^{84}\text{Kr}^{++}$ resulting from a krypton contamination in the tank nitrogen, since the commercial production involves the fractional distillation of liquid air.

Extensive study of the increase in the 42^+ and 56^+ as a function of source pressure was undertaken. The source pressure was monitored by observing the 29^+ ion current. It was found that the 42^+ varied linearly with the pressure and that the 56^+ varied linearly with the square of the pressure. Neither the change in charge mechanism^{2,3} nor the ion-molecule collision mechanism^{4,5} explains both of the observations, although the ion-molecule collision mechanism fully accounts for the presence and behavior of the 56^+ .

Since we were using 70-volt electrons, which is below the appearance potential of $^{28}\text{N}_2^{+++}$, the change in charge mechanism cannot be used to explain the presence of the ion current at mass 42. The present ion-molecule mechanism is inadequate since this current varied linearly with the first power of the pressure. We suggest that this ion current was caused by $^{42}\text{N}_3^+$ produced by a reaction which occurs on the surfaces of the source somewhere in the region of the electron gun. The reaction is zero order with respect to the adsorbed species and first order with respect to the species in the gas phase.

The following observations on a 1:1 mixture of pure $^{28}\text{N}_2$ and pure $^{30}\text{N}_2$ are consistent with our postulates. The 42^+ , 43^+ , 44^+ (uncertain due to high background) and 45^+ ion currents were observed to increase linearly with the pressure which corresponds to the formation of N_3^+ by some surface mechanism. The 56^+ , 58^+ and 60^+ increased linearly with the square of the pressure, which corresponds to a collision of gas phase molecules and/or ions.

These observations of N_3^+ and N_4^+ are not forbidden by the generally accepted hypothesis which proposes a low probability of endothermic reactions^{4,6} occurring in the mass spectrometer.

(2) J. Mattauich and H. Lichtblau, *Physik. Z.*, **40**, 16 (1939).

(3) F. J. Norton, Natl. Bur. Standards Circ. No. 522, pp. 201-204 (1953).

(4) F. H. Field and J. L. Franklin, "Electron Impact Phenomena and the Properties of Gaseous Ions," Academic Press, New York, N. Y., 1957, pp. 217-219.

(5) J. A. Hornbeck and J. P. Molnar, *Phys. Rev.*, **84**, 621 (1951).

(6) F. H. Field and F. W. Lampe, *THIS JOURNAL*, **79**, 4244 (1957).

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THE SEPARATION OF ORTHOHYDROGEN AND PARAHYDROGEN

Sir:

We have found that orthohydrogen and parahydrogen can be separated¹ by gas-adsorption

(1) E. W. Becker, H. Henkes and U. Seifert, *Z. physik. Chem. (Frankfurt)*, **8**, 90 (1955), have reported a very slight enrichment in orthohydrogen by thermal diffusion and demonstrated that K. Schäfer and H. Corte, *Naturwissenschaften*, **33**, 92 (1946), who claimed a greater degree of separation by the same method were in error.

chromatography. Activated alumina columns (swept with nitrogen for 35 min. at $190\text{--}200^\circ$) operated at 77°K . employing purified helium as the carrier gas give sharp separation of these nuclear spin isomers (Fig. 1). The gas stream from the column was passed through a short combustion tube (35-48 mesh copper oxide, 750°) before entering a thermal conductivity cell held at 100° . Signal amplification resulted from the oxidation of hydrogen to water.

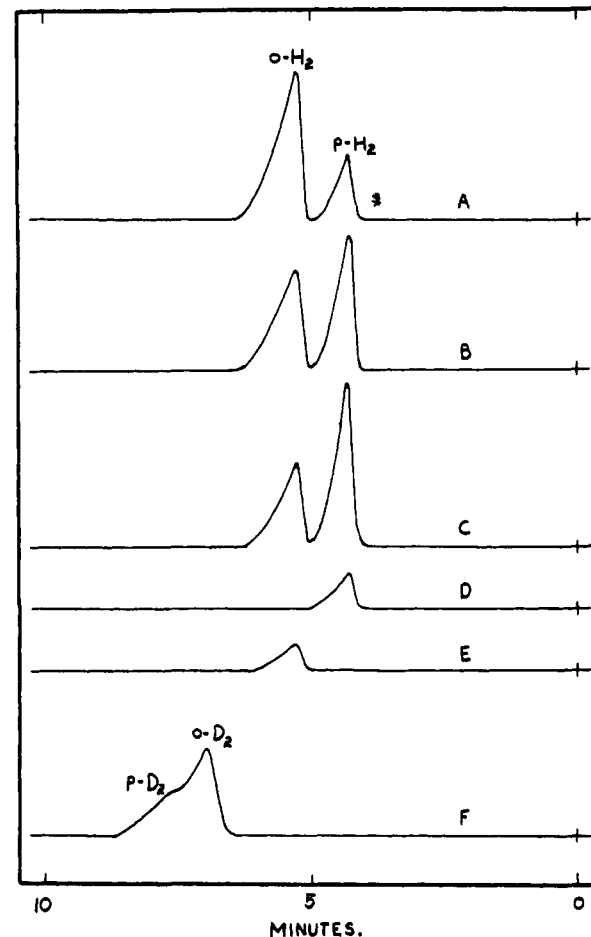


Fig. 1.—Chromatograms of samples of hydrogen and deuterium on an alumina column (150-200 mesh, 120×0.5 cm.; 77.4°K .; helium flow, 240 cc./min.): (A) 1.5 cc. of normal hydrogen; (B) 1.5 cc. of hydrogen equilibrated at 77.4°K .; (C) 1.5 cc. of hydrogen equilibrated at 64°K .; (D) parahydrogen and (E) orthohydrogen obtained by chromatographing 28-cc. samples of the eluent gas withdrawn from each of the two peaks produced by 6 cc. of hydrogen; (F) 1.0 cc. of deuterium.

Since the peak area ratios represent mole ratios, the positive identification of each isomer is demonstrated clearly by the results of analyses of samples of hydrogen equilibrated² at different temperatures (Table I).

The homogeneity of the separated components was shown by sampling the gas stream from the column (ahead of the combustion tube) at the peak maximum for each isomer. Each component,

(2) A. Farkas, "Orthohydrogen, Parahydrogen and Heavy Hydrogen," Cambridge University Press, London, 1935, p. 30.

TABLE I
CHROMATOGRAPHIC ANALYSES OF HYDROGEN

Equilibration temp., °K.	Found	Ortho:Para Ratio Calcd. ³	Fig. 1
~300	3.04 ± 0.15	3.00	A
77.4	0.97 ± 0.05	0.99	B
64	0.66 ± 0.03	0.63	C

as a dilute helium solution, was rechromatographed to check the retention time and purity (Fig. 1, D and E).

With a properly activated column, there is no detectable "irreversible adsorption." When samples of hydrogen were injected slowly between the end of the chromatographic column and the combustion tube using a syringe driven at constant speeds, the areas of the resultant rectangular peaks were the same ($\pm 3\%$) as the sums of the areas of the ortho- and parahydrogen peaks produced when samples of identical size were injected at the front of the column.

That substantial separation of ortho- and para-deuterium occurs is shown by the shoulder on the trailing edge of the deuterium peak (Fig. 1, F). The peak assignment is based upon the ortho:para ratio of 2.00 for normal deuterium. The deuterium isomers are separated completely from the hydrogen isomers; however, orthohydrogen is eluted only slightly more rapidly than HD.

To aid in the interpretation of these separations, we are in the process of measuring chromatographically the heats of adsorption.

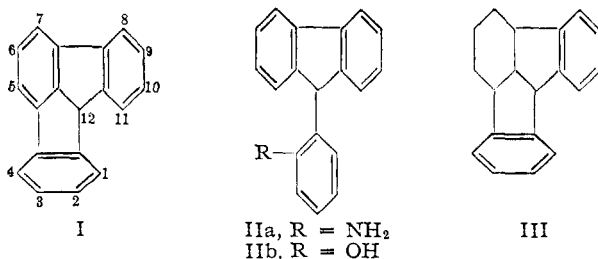
(3) Ref. 2, p. 14.

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FLUORADENE (INDENO[1,2,3-jk]FLUORENE), AN UNUSUALLY ACIDIC HYDROCARBON

Sir:

In continuation of our study of cyclopentindene compounds^{1,2} we wish to report the synthesis and some of the properties of fluoradene (indeno [1,2,3-jk]fluorene) (I) [m.p. 129.8-130.3°. *Anal.* Calcd. for C₁₉H₁₂: C, 95.0; H, 5.0; mol. wt., 240. Found: C, 94.8; H, 4.9; mol. wt. (Rast) 235], prepared in 23% yield by deamination of IIa.³ As



- (1) H. Rapoport and J. Z. Pasky, *THIS JOURNAL*, **78**, 3788 (1956).
(2) H. Rapoport and G. Smolinsky, *ibid.*, **79**, 5831 (1957).
(3) It is of interest to note that a recent attempt to prepare I from 9-(*o*-aminophenyl)-9-fluorenone by deamination led to tribenzotropone as the only product in addition to the phenol [M. Stiles and A. J. Libbey, Jr., *J. Org. Chem.*, **22**, 1243 (1957)].

was anticipated, the presence of two additional fused benzene rings led to a more highly strained system in fluoradene than was present in the parent 2,2a,3,4-tetrahydro-1H-cyclop[cd]indene.¹ Of particular interest is the unusually strong acidity of the hydrogen on C₁₂.

The structure of fluoradene was established (1) by its method of synthesis, (2) by elementary analyses and molecular weight determinations, and (3) in particular by its ease of hydrogenation and consumption of perbenzoic acid, reactions which are characteristic for such strained, fused ring compounds.^{1,2} The hexahydrofluoradene (III) [m.p. 118.4-119.4. *Anal.* Calcd. for C₁₉H₁₈: C, 92.6; H, 7.4. Found: C, 92.5; H, 7.2] resulted from a rapid 300 mole % hydrogen absorption in methanol at room temperature in the presence of palladized carbon. Its ultraviolet spectrum was that of two 1,2- or 1,3-dialkylindanes,⁴ and this lends strong support to the structural assignment. At room temperature, fluoradene (I) consumed 400 mole % of perbenzoic acid while under the same conditions 9-phenylfluorene consumed 50 mole %. Both of these reactions reflect the presence of appreciable strain in the benzene ring which is doubly-fused to five-membered rings.

The most unusual property of fluoradene is the acidity of the one remaining non-aromatic hydrogen at C₁₂. This was first observed when it was discovered that fluoradene could be removed from benzene by washing with dilute aqueous alkali and was confirmed by exchanging this hydrogen for deuterium in boiling deuterium ethoxide, conditions under which 9-phenylfluorene shows no exchange. In alkaline solution fluoradene develops a pink color reminiscent of phenolphthalein. On acidification, fluoradene is recovered, but in the presence of oxygen the color fades and 12,12'-bifluoradenyl is formed [m.p. 306-307 dec. *Anal.* Calcd. for C₃₈H₂₂: C, 95.4; H, 4.6. Found: C, 95.4; H, 4.7.], identical with the product from the reaction of 12-bromofluoradene with mercury. To obtain a quantitative measure of this acidity, the distribution of fluoradene was examined between hexane and 97% aqueous methanol as a function of pH. By this procedure, a *pK'*_a of 11 ± 0.5 (extrapolated to water) was found for fluoradene.⁵ This is a truly remarkable acidity and should be compared with the most acidic hydrocarbons heretofore known, 9-phenylfluorene, phenylacetylene, and indene,⁶ for which *pK'*_a's of 21 or greater have been reported. Undoubtedly, the high symmetry and complete conjugation in the fluoradene anion are responsible for this extreme acidity.

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(4) J. Entel, C. H. Ruoff and H. C. Howard, *Anal. Chem.*, **25**, 1303 (1953).

(5) The same method applied to 9-(*o*-hydroxyphenyl)-fluorene (IIb) led to a *pK'*_a of 12.2 in 97% aqueous methanol. In water, this phenol has a *pK'*_a of 9.7, and the difference, 2.5 *pK* units, was used for the extrapolation of fluoradene's acidity to water.

(6) J. B. Conant and G. W. Wheland, *THIS JOURNAL*, **54**, 1212 (1932); W. K. McEwen, *ibid.*, **58**, 1124 (1936).