Our calculated value for the pre-exponential factor is $4 \times 9.2 \times 10^{12} = 3.7 \times 10^{13}$ cc. mole^{-1} sec.$^{-1}$. The agreement is all that one should expect.

We may conclude that the pre-exponential factors in these reactions with chlorine atoms are in accord with the transition state theory. Also we found that the classical partition function yielded a good approximation for the reactions of hydrocarbons with chlorine atoms. The extension of this method to cases of other reactions of a single atom with a molecule is straightforward and will yield similar simplification of the calculations. Extension of the classical partition function to reactions between two diatomic or polyatomic molecules (or radicals) is also quite feasible.

BERKELEY, CAL.

[CONTRIBUTION FROM THE PHYSICAL RESEARCH DIVISION, CHEMICAL WARFARE LABORATORIES]

Nuclear Magnetic Resonance Spectra of Some Fluorocarbon Derivatives

BY NORBERT MULLER,[1] PAUL C. LAUTERBUR AND GEORGE F. SVATOS

RECEIVED DECEMBER 6, 1956

The ^{19}F nuclear magnetic resonance (NMR) spectra of a number of perfluoroörganic compounds have been measured. Correlations are presented between the observed chemical shifts and the types of fluorine-containing groups present. Interpretation of the spectra often is facilitated by observing the fine structures of the resonance signals. NMR spectroscopy is an excellent source of information as to the structures and purities of new fluorocarbon derivatives.

Introduction

The usefulness of nuclear magnetic resonance (NMR) spectroscopy in determining the structures of organic and fluorocarbon molecules is now widely recognized. It is based on the fact that the chemical shift of the resonance from a proton or an F^{19}-nucleus is determined by the nature of the functional group in which the nucleus is found, although there is some overlapping of the regions containing the resonances associated with different groups. Meyer, Saika and Gutowsky[2] observed proton resonances from a large variety of organic materials, and present extensive correlations between the chemical shifts found and the natures of the proton-containing groups. As yet there is very little analogous work in the literature concerning F^{19} chemical shifts.[3-5] We are therefore presenting this account of the application of NMR spectroscopy to the identification and determination of the structures of a number of perfluoroörganic compounds prepared in these laboratories.[6]

Experimental

The apparatus used in this work differs from that previously described[7] only in that a Varian Model V-K 3506 super-high resolution field stabilizing unit has been added. The effects of field inhomogeneities were reduced by using Varian Associates' spinning attachment. The resolution obtained is illustrated in Fig. 1; the separation between the most closely spaced components of the multiplet shown is just under one milligauss.

Chemical shifts were measured by the "side-bands" technique,[8] using CF_3COOH as the source of the standard resonance. The unit employed is

$$\delta = \frac{(H_s - H_r)}{H_r} \times 10^6$$

where H_s and H_r are the resonant magnetic fields for the sample and the reference compound, respectively.[9] The measured values were reproducible to within 0.1 δ-unit, and are not corrected for bulk-diamagnetic effects.[10]

The preparations and purifications of the samples are described in reference 6. All were examined at room temperature, as liquids sealed in Pyrex tubes of 5 mm. outside diameter which were filled to a height of about 25 mm.

Results and Discussion

Assignment of the Resonances.—The δ-values of the resonances of the various fluorine-containing groups of each molecule studied are given in Table I, and the correlation between chemical shifts and types of group is summarized in Table II. The assignments were made on the basis of the fact that similar groups in different compounds should give resonances in the same region, and also the rule that the intensity of each signal is proportional to the number of resonating nuclei. The absence of any resonances which could not be accounted for in this manner is strong evidence in favor of the structures proposed for the compounds, and also indicates that at most a few mole per cent. of fluorine-containing impurities could have been present, since the possibility of a sample's containing several compounds with identical NMR spectra is rather remote. In several cases the observed spectrum formed the basis for a choice between several candidate structures.

Indirect Spin-Spin Interactions.—In a number of instances, the assignments could be confirmed by observation of the hyperfine structure resulting

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(1) Department of Chemistry, Purdue University, Lafayette, Indiana.

(2) L. H. Meyer, A. Saika and H. S. Gutowsky, THIS JOURNAL, **75**, 4567 (1953).

(3) S. Steinle, H. M. McConnell and others, volume 2 of Final Report on Contract No. CML-4564, Shell Development Company, Emeryville, California, 1954.

(4) (a) H. S. Gutowsky, D. W. McCall, B. R. McGarvey and L. H. Meyer, THIS JOURNAL, **74**, 4809 (1952); (b) J. N. Shoolery, *Anal. Chem.*, **26**, 1400 (1954).

(5) G. V. D. Tiers, THIS JOURNAL, **78**, 2914 (1956).

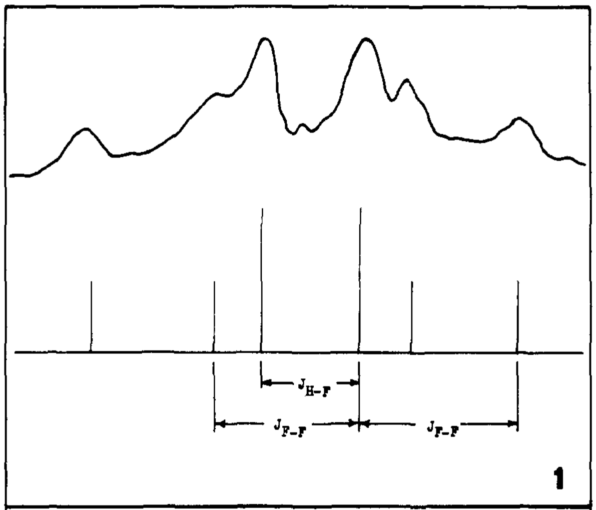
(6) J. A. Young, T. C. Simmons and F. W. Hoffman, *ibid.*, **79**, in press (1957); F. W. Hoffman, T. C. Simmons, *et al.*, presented at the 130th National Meeting of the Am. Chem. Soc.; R. J. Koshar, T. C. Simmons and F. W. Hoffman, presented at the 130th National Meeting of the Am. Chem. Soc.; T. C. Simmons, F. W. Hoffman, *et al.*, in preparation.

(7) N. Muller, P. C. Lauterbur and G. F. Svatos, to be published.

(8) J. T. Arnold and M. E. Packard, *J. Chem. Phys.*, **19**, 1608 (1951); see also N. Muller, P. C. Lauterbur and J. Goldenson, THIS JOURNAL, **78**, 3557 (1956).

(9) There is as yet no universally adopted convention as to the definition of δ; chemical-shift scales are in use in which the sign of the δ's is reversed, and for which different origins have been chosen. See, for example, the discussion in reference 4b.

(10) W. C. Dickinson, *Phys. Rev.*, **81**, 717 (1951).



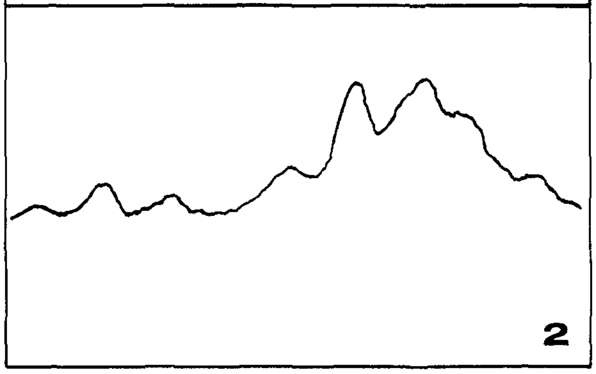


Fig. 1.—Multiplet structure of the CF_3 resonance from $(CF_3)_2CHCF_2OCH_3$. The resonance is split into a triplet by the interaction with the CF_2 groups (J_{F-F} = 10.9 cps.). Each component is further split into a doublet by the coupling with the CH group (J_{H-F} = 7.4 cps.).

Fig. 2.—Partially resolved hyperfine structure of the CF_3 resonances from $(CF_3)_2C{=}CFOCH_3$. The two CF_2 groups are chemically distinct and give rise to separate resonances. These are split by spin–spin coupling with each other, as well as by coupling with the CF fluorine.

from indirect spin–spin coupling.[11] Such information is also summarized in Table I. The resolved hyperfine patterns were all of the form predicted from the number and statistical weights of the possible spin states of neighboring groups.

An example is the resonance of the CF_3 groups of $(CF_3)_2CHCF_2OCH_3$, shown in Fig. 1. Surprisingly, the strongest interaction (coupling constant, J = 10.9 cycles/sec.) is that between the CF_3 and CF_2 groups, which splits the CF_3 signal into a symmetrical triplet. Each component of the triplet is split into a doublet by the coupling with the CH proton (J = 7.4 cycles/sec.), and perhaps somewhat broadened by interaction with the CH_3 protons, though coupling over such a large distance would probably be very feeble.

Unresolvable hyperfine structure, as was found for a number of resonances, may arise in a variety of ways. In the saturated fluorocarbons, the coupling constants are usually too small to give a resolvable splitting. In other molecules, resolution may be prevented either because of the overlapping of independent multiplets, or because resonances are split by several nearby groups with unequal coupling constants, or again because of the complex nature of the coupling which is to be expected when the coupling constants are comparable with the difference in chemical shifts between the interacting groups.[7,12]

An example is the partially resolved structure found for the CF_3 groups of $(CF_2)_2C{=}CFOCH_3$, shown in Fig. 2. The two CF_3 groups are chemically distinct, one being *cis* and the other *trans* to the OCH_3 group. Hence they interact with each other, as well as with the =CF fluorine; the latter can be expected to split both CF_3 multiplets, but not to the same extent. Thus the observed pattern results from the superposition of not less than sixteen distinct components.

Further Discussions. The Fluorocarbons.—The resonances of the small number of fluorocarbons included in this study fall into three, well separated regions, corresponding to C–CF_3 groups (δ = −14 to +6), C–CF_2–C groups (δ = +35 to 55) and $\begin{matrix}C\\C\end{matrix}\!\!>$CF–C groups ($\delta$ = +107 to 113.) This is in keeping with the idea[4b,13,14] that with our definition of δ a positive shift implies a relatively high electron density around the ^{19}F-nucleus, and that the amount of charge which each fluorine is able to draw from a carbon atom decreases as the number of competing fluorines bound to that carbon increases.

Within each range, the δ-value evidently depends on the nature of the atoms or groups bonded to the neighboring carbons. These variations are not easily interpretable. For example, since a fluorine atom should be much more effective in withdrawing electrons than a –CF_3 group,[5] it is puzzling to find greater shielding in the –CF_3 groups of $(CF_3)_3CF$ than in those of $(CF_3)_4C$. Possibly this may involve a "repulsive unshielding" effect of the kind proposed by Tiers.[5]

The Nitrogen-containing Compounds.—Again in the nitrogen-containing compounds the chemical shifts are roughly as expected from the relative electronegativities of the atoms involved. Thus C–NF–C groups show shifts that are about seventy units more negative than those in $\begin{matrix}C\\C\end{matrix}\!\!>$CF–C, and –$CF_2$– or –$CF_3$ groups adjacent to nitrogen have more negative δ's than those in the normal fluorocarbons. (The same is true of –CF_2– groups adjacent to oxygen, where these occur.) Once again, some of the shifts are puzzling; in $CF_3CF_2CF_2NF_2$, for example, the two CF_2 resonances can be assigned[15] by their hyperfine structures, and the one

[11] H. S. Gutowsky, D. W. McCall and C. P. Slichter, *J. Chem. Phys.*, **21**, 279 (1953).

[12] (a) E. L. Hahn and D. E. Maxwell, *Phys. Rev.*, **88**, 1070 (1952); (b) H. M. McConnell, A. D. McLean and C. A. Reilly, *J. Chem. Phys.*, **23**, 1152 (1955).

[13] H. S. Gutowsky and C. J. Hoffman, *ibid.*, **19**, 1259 (1951).

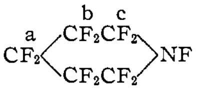
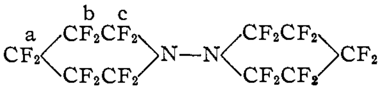
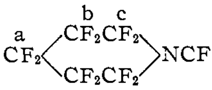
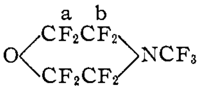
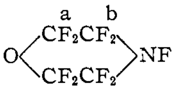
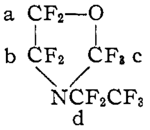
[14] A. Saika and C. P. Slichter, *ibid.*, **22**, 26 (1954).

[15] These assignments are perhaps incorrect. As pointed out by a referee, the results of reference 16 suggest that the quadruplet may correspond to the CF_2 group nearest the NF_2 and the triplet to the one nearest the CF_3; this is the reverse of what would normally have been

TABLE I

^{19}F NUCLEAR MAGNETIC RESONANCE SPECTRA OF ORGANOFLUORINE COMPOUNDS

$$\delta = \frac{(H_{\text{sample}} - H_{CF_3COOH})}{H_{CF_3COOH}} \times 10^6$$

Formula	Group	δ	Obsd. spin–spin coupling
1. Fluorocarbons			
$(CF_3)_4C$	CF_3	−13.8	None
$(CF_3)_3CF$	CF_3	− 1.2	Doublet
	CF	112.5	[a]
$CF_3CF_2CF_2CF_3$	CF_3	6.0	Triplet
	CF_2	51.4	[a]
$\overset{a}{CF_3}\overset{b}{CF_2}\overset{c}{CF_2}CF(\overset{d}{CF_2}\overset{e}{CF_3})_2$	CF_3(a)	4.8	Triplet
	CF_3(e)	3.2	[a]
	CF_2(b)	46.6	[a]
	CF_2(c)	34.4	[a]
	CF_2(d)	37.4	[a]
	CF	107.0	[a]
Perfluorocyclohexane	CF_2	55.0	None
2. Alkoxy derivatives of perfluoroisobutylene			
$(CF_3)_2CHCF_2OCH_3$	CF_3	−12.8	See Fig. 1
	CF_2	− 3.0	[a]
$(CF_3)_2C{=}CFOCH_3$	CF_3	−18.9	See Fig. 2
	CF	− 9.4	[a]
$(CF_3)_2C{=}CFOCH_2CH_2CH_3$	CF_3	−19.7	See Fig. 2
	CF	−11.8	[a]
$(CF_3)_2C{=}C(OCH_2CH{=}CH_2)_2$	CF_3	−11.1	None
$(CF_3)_2CHCF_2OCH_2CH_2F$	CF_3	−13.0	See Fig. 1
	CF_2	− 6.2	[a]
	CF	149.5	[a]
$(CF_3)_2C{=}\overset{a}{CF}OCH_2\overset{b}{CH_2F}$	CF_3	−19.3	See Fig. 2
	CF(a)	−11.1	[a]
	CF(b)	149.5	[a]
3. Nitrogen-containing compounds			
A. Cyclic			
	CF_2(a)	56.7	[a]
	CF_2(b)	54.5	[a]
	CF_2(c)	32.7	[a]
	NF	36.6	[a]
	CF_2(a)	56.2	[a]
	CF_2(b)	55.3	[a]
	CF_2(c)	19.1	[a]
	CF_2(a)	57.8	[a]
	CF_2(b)	55.2	[a]
	CF_2(c)	16.8	Quadruplet
	CF_3	−25.3	Quintuplet
	CF_2(a)	9.6	[a]
	CF_2(b)	17.0	Quadruplet
	CF_3	−24.0	Quintuplet
	CF_2(a)	4.8	[a]
	CF_2(b)	33.7	[a]
	NF	36.0	[a]
	CF_2(a)	14.9	[a]
	CF_2(b)	22.2	Quintuplet
	CF_2(c)	−20.6	[a]
	CF_2(d)	8.6	Quintuplet
	CF_3	10.6	Triplet
B. Non-cyclic			
$(\overset{a}{CF_3}\overset{b}{CF_2}\overset{c}{CF_2}\overset{d}{CF_2})_2N\overset{e}{CF_3}$	CF_3(a)	5.0	Triplet
	CF_3(e)	−26.5	[a]
	CF_2(b)	25.0	[a]
	CF_2(c)	21.9	[a]
	CF_2(d)	10.0	[a]
$(\overset{a}{CF_3}CF_2)_2N\overset{b}{CF_3}$	CF_3(a)	7.7	[a]
	CF_3(b)	−25.3	[a]
	CF_2	16.8	[a]
$CF_3\overset{a}{CF_2}\overset{b}{CF_2}NF_2$	CF_3	6.4	Triplet
	CF_2(a)	27.1	Quadruplet
	CF_2(b)	51.1	Triplet
	NF_2	−92.0	[a]
$(CF_3)_2NC(O)F$	CF_3	−20.0	Doublet
	CF	−81.0	Septet
$(CF_3)_2NC(O)N(CF_3)_2$	CF_3	−20.4	None
$(CF_3)_2CHC{\equiv}N$	CF_3	−10.6	Doublet
$\overset{a}{CF_3}\overset{b}{CF_2}\overset{c}{CF_2}CF{=}N\overset{d}{CF_3}$	CF_3(a)	5.2	Triplet
	CF_3(d)	−36.2	Doublet
	CF_2(b)	42.4	Quintuplet
	CF_2(c)	51.4	Doublet
	CF	−52.7	[a]
$CF_2{=}NCF_3$	CF_3	−18.8	[a]
	CF	−44.6	Doublet
	CF	−25.2	Doublet
$HN(CH_2CH_2F)_2$	CF	145.5	[a]
4. Miscellaneous compounds			
CF_3CF_2COOH	CF_3	7.0	[a]
	CF_2	46.0	[a]
$(CF_3CF_2)_2O$	CF_3	11.9	[a]
	CF_2	12.9	[a]

[a] Resonances somewhat broadened by spin–spin interaction, but not resolved into discrete components.

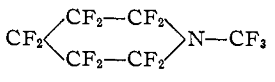
TABLE II

Group	No. obsd.	Range of δ's found
CH_2CH_2F	3	149.5 to 145.5
C_3CF	2	112.5, 107.0
C–CF_2–C	17	57.8 to 21.9
C–CF_2–N	10	51.1 to 8.6
C–NF–C	2	36.6, 36.0
C–CF_2–O	6	14.9 to −6.2
$\overset{*}{CF_3}$–CF_2–[a]	10	11.9 to 3.2
All other CF_3–C	10	0.0 to −19.7
C=CF–O	3	−9.4 to −11.8
CF_3–N	9	−18.8 to −36.2
O–CF_2–N	1	−20.6
CF_2=N	1	−25.2 and −44.6
C–CF=N	1	−52.7
N–C(O)F	1	−81.0
C–NF_2	1	−92.0

[a] The asterisk indicates which group is meant.

from the group next the NF_2 proves to have a more positive δ than the one next to the CF_3.

Another striking effect is the unexpectedly strong spin–spin coupling found between fluorines separated by a C–N–C group, as in $R'_FN(R_F)_2$. Thus the CF_3 resonance in such compounds as



is resolved readily into a quintet, although the resonances in, for example, CF_3CF_2COOH cannot be resolved at all. Quantitative measurements of the coupling constants were not made.[16]

Fluorines separated by C=N–C bridge appear to be somewhat less strongly coupled; in CF_2=N–CF_3 the two fluorines of the CF_2 group are nonequivalent, and give rise to a pair of doublets. No further splitting, such as would result from interaction of the CF_2 and CF_3 fluorines, was resolved.

Finally, the compound C_3F_7CF=NCF_3 is of in-

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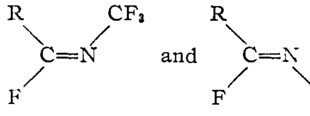
expected. Similar considerations may affect the assignments of the (b) and (c) CF_2 groups for $CF_3CF_2CF_2CF{=}NCF_3$ given in Table I.

[16] This effect has recently been discussed by A. Saika and H. S. Gutowsky, THIS JOURNAL, **78**, 4818 (1956).

terest because one would expect its spectrum to correspond to a mixture of the two isomeric forms



The N–CF_3 resonance proved to be a doublet, with separations of the components, in cycles/sec., approximately the same at 17 mc. (about 4,200 gauss) as at 40 mc. The doublet splitting must therefore be due to spin–spin coupling, leading to the inference that either the two forms have the same resonance spectrum or, as seems more probable, the preparation and purification[6] yielded an essentially isomerically pure product. If the latter is true, the data still do not suffice to show which of the two forms was present.

ARMY CHEMICAL CENTER, MD.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, HARVARD UNIVERSITY]

The Infrared Spectrum of Cuprous Chloride Vapor

BY WILLIAM KLEMPERER, STUART A. RICE AND R. STEPHEN BERRY

RECEIVED SEPTEMBER 24, 1956

The infrared spectrum of cuprous chloride vapor in equilibrium with the liquid has been measured from 500 to 220 cm.$^{-1}$. One strong absorption with maximum at 350 cm.$^{-1}$ was observed. The observed spectrum is in agreement with the existence of a cyclic polymer as the principal species in the vapor. The bonds of the polymer are considerably weaker than those in the diatomic monomer.

Diverse experiments indicate that cuprous chloride vapor in equilibrium with the liquid phase consists primarily of polymeric species. Vapor density measurements of Brewer and Lofgren[1] are consistent with the existence of a single polymer-monomer equilibrium, namely, trimer–monomer. If it is assumed that the trimer has a cyclic structure then the thermal data of the above authors indicate the trimer to have an average bond energy of 2.8 e.v. as compared to 3.8 e.v. in the monomer. Since there is in general a rough correlation between bond energy and bond stretching force constant it appears that information concerning the type of bonding present in the trimer can be obtained from a study of the infrared spectrum of the trimeric molecule.

The experimental technique is similar to that used in previous studies.[2,3] The temperature at which cuprous chloride has appreciable vapor pressure is low enough (approximately 1000°) to permit the use of a relatively simple furnace and cell. The furnace used is an aluminum oxide tube wound with Kanthal A-1 resistance wire. The cell is a 1.5 meter Vycor tube 45 mm. in diameter. The cell windows are polyethylene and nitrogen is used as inert gas to prevent condensation of the hot vapors on the windows which are at room temperature.

Although it is possible to study either the absorption or emission spectrum of a substance with the above apparatus, as previously discussed,[3] emission studies suffer from much self-absorption and from the presence of radiation from the hot cell walls. This latter radiation can be removed only by reducing the aperture of the optical system, with the concurrent loss in spectral resolution. Since absorption studies do not suffer from these shortcomings they were used principally. For absorption studies it is necessary to modulate the light before is passes through the sample since the sample is at about the same temperature as the light source.

The spectrum was observed with a Perkin–Elmer Model 12 monochromator using cesium bromide and cesium iodide optics in the spectral region 500 to 200 cm.$^{-1}$. Only one intense absorption was observed with a maximum at 350 cm.$^{-1}$. There was no noticeable absorption around the region of 420 cm.$^{-1}$.

In cuprous chloride a well developed spectrum was observed when the sample was at approximately 900°, while for cuprous bromide no definite absorption or emission was detected at temperatures up to 1400°. In the course of the studies on cuprous bromide the Vycor tube melted and in view of the reactivity of cuprous bromide with steel no other easily available cell could be used. Therefore it was not possible to measure the spectrum of cuprous bromide with the present apparatus.

Results and Discussion

The observed spectrum of cuprous chloride is in full agreement with previous work on the presence of a polymeric molecule in the gas in equilibrium with the liquid. There is no evidence of any absorption by the monomer CuCl, whose vibration frequency is 416.9 cm.$^{-1}$[1,4] at pressures where the previously mentioned 350 cm.$^{-1}$ absorption is well developed. It is impossible to make arguments for this large displacement of the absorption maximum from the vibration frequency due to hot transitions since the anharmonicity is only 1.6 cm.$^{-1}$. Furthermore, in a diatomic molecule in a $^1\Sigma$ electronic state the effects of rotational structure and anharmonicity approximately cancel so that the resulting absorption maximum lies near the true vibration frequency.[3] The absorption with maximum at 350 cm.$^{-1}$ is thus attributed to the polymer of cuprous chloride.

The observed spectrum, namely, a single bond stretching motion, is consistent with a cyclic structure for the polymer. In the case of an open chain one would expect two types of stretching motions of widely different frequencies corresponding, re-

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(1) L. Brewer and N. L. Lofgren, THIS JOURNAL, **72**, 3038 (1950).

(2) W. Klemperer, *J. Chem. Phys.*, **24**, 353 (1956).

(3) W. Klemperer and S. A. Rice, *ibid.*, in press.

(4) G. Herzberg, "The Spectra of Diatomic Molecules," 2nd edition, D. Van Nostrand, New York, N. Y., 1950.