for all colloidal electrolytes tested, whether the fastest ion is the relatively slow sodium or the highly mobile hydrogen ion. It is as though the mobility of the colloid adjusted itself to that of the gegen ion. Reference to Fig. 4 shows a qualitative parallel between the observations made here and Brady's observations. The steeper of the two straight lines, corresponding to the more mobile of two cations, intercepts the hyperbolas at a higher point, the point of intersection determining the contribution of the "hyperbolic" part to the total conductivity. If the "hyperbolic" part corresponds to conducting micelles, the latter automatically adjust their contribution to the mobility of the gegen ion as a necessary consequence of equation (1).

TABLE II

COMPARISON OF CALCULATED THEORETICAL MAXIMUM AND OBSERVED CONDUCTIVITY AT THE $C_{\text{min.}}$ (BRADY)

| Substance | $\alpha_{\text{calcd.}} = \Lambda_{\text{calcd.}}/\Lambda_0$ | $\alpha_{\text{obs.}} = \Lambda_{\text{obs.}}/\Lambda_0$ | $\alpha_{\text{obs.}}/\alpha_{\text{calcd.}} = \Lambda_{\text{obs.}}/\Lambda_{\text{calcd.}}$ |
|---|---|---|---|
| Lauryl sulfonic acid | 0.317 | 0.390 | 1.24 |
| Catol 607 | .287 | .371 | 1.29 |
| Potassium laurate | .389 | .507 | 1.30 |

Since the specific conductivity, *L*, being based on a fixed volume of solution, directly reflects changes of concentration and mobility of the conducting species present in the solution, it is worth noting that from equation (1) one gets

$$\Lambda C = 1000L = AC^{1/2} + BC^{3/2} \qquad (5)$$

Thus colloidal electrolytes in the region under discussion behave as though the conductivity were due to two ionic species, the mobility–concentration product of one of which is increasing with the square root and that of the other as the three-halves power of the solute concentration.

Our present knowledge of colloidal electrolytes does not permit an interpretation of these facts in terms of chemical equations consistent with all available data. Therefore, for the present, it is safer to regard this as purely formal analysis, which, however, must have a physical basis.

**Acknowledgment.**—The author wishes to express his sincere thanks to Professor J. W. McBain for his valuable assistance and suggestions in the preparation of this manuscript.

## Summary

1. The equivalent conductivity of the majority of colloidal electrolytes, in the region of the conductivity minimum, has been shown to follow the law: $\Lambda = A/\sqrt{C} + B\sqrt{C}$, where *A* and *B* are constants depending primarily upon anion and cation, respectively.

2. The minimum in the conductivity curve occurs at a concentration equal to $A/B$.

3. The two parts of the equivalent conductivity, $A/\sqrt{C}$ and $B\sqrt{C}$, are equal when the conductivity is at its minimum.

STANFORD UNIVERSITY, CALIFORNIA

RECEIVED MARCH 5, 1945

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AT THE OHIO STATE UNIVERSITY]

# The Synthesis and Directed Chlorination of 2,2-Difluorobutane

BY ALBERT L. HENNE AND JAMES B. HINKAMP

The chlorination of $CF_3CH_2CH_3$, $CH_3CF_2CH_3$, and $CH_3CFClCH_2Cl$ is known to be strongly directed.[1] To determine how far and in what direction the effect of a $CF_2$ group would extend, $CH_3CF_2CH_2CH_3$ was synthesized and chlorinated.

The difluoromethane was obtained by hydrofluorination of $CH{\equiv}CCH_2CH_3$,[2,3] and also by the action of hydrogen fluoride upon $CH_3CCl{=}CHCH_3$,[3,4] $CH_2{=}CClCH_2CH_3$ and $CH_3CFClCH_2CH_3$. Since large amounts of reagents were handled, the experimental procedures were modified as follows, for the protection of the operator.

A five-liter, three-necked steel cylinder was fitted with a copper Dry Ice reflux condenser, a stirrer, and a copper inlet tube reaching the bottom. A quantity of commercial 70% $CH_3CCl{=}CHCH_3$ corresponding to 22 moles of the pure compound was placed in the cylinder, and a stream of hydrogen fluoride was led through it. The reaction started at once, and as soon as it was well under way a large ice-bath was placed around the vessel. The reaction was conducted as fast as the capacity of the reflux condenser would allow. The hydrogen chloride discharged from the top of the condenser was absorbed in water. After feeding about one hundred moles of hydrogen fluoride (slightly more than twice the amount needed) the reaction mixture was stirred for two hours at room temperature. The reflux condenser was replaced by a scrubber containing continuously changed hot water, attached to an ice-cooled receiver. The steel vessel was progressively heated to 90° to boil off the reaction products. After washing, drying and fractionally distilling, the distillate gave 11.3 moles (1062 g. or 51.3% yield) of pure $CH_3CF_2CH_2CH_3$ and about 8% of intermediate $CH_3CFClCH_2CH_3$ from which more difluoride was obtained by subjecting to a

---

[1] (a) Henne and Whaley, THIS JOURNAL, **64**, 1157 (1942); (b) Henne and Renoll, *ibid.*, **59**, 2434 (1937); (c) Henne and Haeckl, *ibid.*, **63**, 2692 (1941).

[2] (a) Henne and Plueddemann, *ibid.*, **65**, 587 (1943); (b) Grosse and Linn, *ibid.*, **64**, 2289 (1942).

[3] Henne and Plueddemann, *ibid.*, **65**, 1271 (1943).

[4] Renoll, *ibid.*, **64**, 1115 (1942).

second treatment with hydrogen fluoride, or by adding to a subsequent operation.

### Chlorination

In sunlight, in the presence of water, $CH_3CF_2CH_2CH_3$ gave only two of the possible three monochlorides; two parts of $CH_3CF_2CHClCH_3$ and three parts of $CH_3CF_2CH_2CH_2Cl$ were formed, but not even a trace of $CH_2ClCF_2CH_2CH_3$. The end $CH_3$ adjacent to the $CF_2$ group proved immune to chlorination, while the $CH_2$ adjacent to the $CF_2$ group and the $CH_3$ once removed were affected in proportion to the number of hydrogen atoms available for chlorination, *i. e.*, apparently at random.

On further chlorination, $CH_3CF_2CHClCH_3$ gave two parts of $CH_3CF_2CCl_2CH_3$ to one part of $CH_3CF_2CHClCH_2Cl$, but no $CH_2ClCF_2CHClCH_3$. On the other hand, $CH_3CF_2CH_2CH_2Cl$ gave only $CH_3CF_2CH_2CHCl_2$ without evidence of either $CH_3CF_2CHClCH_2Cl$ or $CH_2ClCF_2CH_2CH_2Cl$, and a continuation of the chlorination gave seven parts of $CH_3CF_2CH_2CCl_3$ to one part of $CH_3CF_2CHClCHCl_2$ and no $CH_2ClCF_2CH_2CHCl_2$. These results illustrate the extent to which the alpha methyl group is protected against chlorine, and they confirm the strong tendency to accumulate the chlorine atoms on the same carbon atom, which had been noted in the propane series.[1]

To complete the study, $CH_2ClCF_2CH_2CH_3$ was synthesized as indicated hereunder, and subjected to chlorination. It failed to give any $CHCl_2CF_2CH_2CH_3$, but gave four parts of $CH_2ClCF_2CH_2CH_2Cl$ to one part of $CH_2ClCF_2CHClCH_3$. This result reinforced the observation that an end group adjacent to a $CF_2$ group resists chlorination. The two dichlorides actually formed were not found to be in proportion to the number of hydrogen atoms available on each carbon, as beta chlorination appeared to be favored.

Finally, chlorination was allowed to proceed to completion and yielded $CCl_3CF_2CCl_2CCl_3$ b. p. 270° with slow decomposition. To accomplish this result, several weeks of exposure to brilliant sunlight at a temperature of about 60° were required.

### Identifications

Most chlorofluorides were identified by comparing their freezing point, boiling point, density and refractive index with those of synthetic samples obtained from the needed polychlorides by fluorination with hydrogen fluoride and mercuric oxide, using the procedures previously reported.[5] The remaining chlorofluorides were then identified by a process of elimination, based on their difference from established compounds.

**$CH_3CF_2CHClCH_3$** was obtained in 35% yield from $CH_3CCl_2CHClCH_3$ (made by chlorine addition to $CH_3CCl{=}CHCH_3$) together with $CH_3CFClCHClCH_3$ in 31% yield. The place of the fluorine atoms was ascertained by perchlorination to the known $CCl_3CF_2CCl_2CCl_3$.

**$CH_2ClCF_2CH_2CH_3$** was obtained in 55% yield from $CH_2ClCCl_2CH_2CH_3$ made in 65% yield by chlorine addition to dry $CH_2{=}CClCH_2CH_3$ in the dark and in the presence of solid sodium bicarbonate.

**$CH_3CF_2CH_2CH_2Cl$** was identified by the fact that it differed from the preceding monochlorides.

$CH_2ClCF_2CHClCH_3$ was obtained in 24% yield from commercial $CH_2ClCCl_2CHClCH_3$,[6] together with 53% of $CH_2ClCClFCHClCH_3$ and 7% of recovered tetrachloride. It was also obtained in 45% yield from $CH_2ClCFClCHClCH_3$ in addition to 29% of recovered material. The place of the fluorine atoms was demonstrated by perchlorination to the known $CCl_3CF_2CCl_2CCl_3$.

**$CH_3CF_2CHClCH_2Cl$** was obtained quantitatively by chlorine addition to $CH_3CF_2CH{=}CH_2$ made in 75% yield by hydrogen chloride removal from $CH_3CF_2CH_2CH_2Cl$.

**$CHCl_2CF_2CH_2CH_3$** was obtained in 40% yield, together with 14% of $CHCl_2CFClCH_2CH_3$ and 15% of unreacted tetrachloride, from $CHCl_2CCl_2CH_2CH_3$ made in 51% yield by chlorine addition to 1-butyne vapors diluted in methylene chloride and in the presence of solid sodium bicarbonate. The position of the fluorine atoms was demonstrated by perchlorination to the known $CCl_3CF_2CCl_2CCl_3$.

**$CH_2ClCF_2CH_2CH_2Cl$** was identified by being a dichloride obtained from $CH_2ClCF_2CH_2CH_3$ and by being different from both $CH_2ClCF_2CHClCH_3$ and $CHCl_2CF_2CH_2CH_3$.

**$CH_3CF_2CH_2CHCl_2$** was identified by being a dichloride formed from $CH_3CF_2CH_2CH_2Cl$ and by being different from both $CH_2ClCF_2CH_2CH_2Cl$ and $CH_3CF_2CHClCH_2Cl$.

**$CH_3CF_2CH_2CCl_3$** was obtained from $CH_3CF_2CH_2CHCl_2$ and was shown to have a $CCl_3$ group by its easy fluorination to $CH_3CF_2CH_2CF_3$, a pentafluoride which was also obtained from $CF_3CH_2CCl_2CH_3$.[7]

**$CH_3CF_2CHClCHCl_2$** was identified by its formation from both $CH_3CF_2CHClCH_2Cl$ and $CH_3CF_2CH_2CHCl_2$.

### Reactivity Tests

The chlorofluorides were treated with an alcoholic solution of silver nitrate to test the ease of replacement of the chlorine atoms. The procedure consisted in treating three to five drops of organic material with 1 ml. of a 5% alcoholic solution of silver nitrate, and boiling for five minutes. Both $CH_2ClCF_2CH_2CH_3$ and $CH_3CF_2CHClCH_3$ failed to give a precipitate, while $CH_3CF_2CH_2CH_2Cl$ gave a faint turbidity. In contrast, this test gives a strong precipitate even at room temperature with $CH_3CF_2CH_2CH_2CH_2Cl$.[8]

---

[5] (a) Henne and Midgley, THIS JOURNAL, 58, 884 (1936); (b) Henne, *ibid.*, 60, 1569 (1938); (c) Henne and Flanagan, *ibid.*, 65, 2362 (1943).

[6] Research Chemicals, San Jose, California.

[7] J. Hinkamp, Dissertation, The Ohio State University, 1943.

[8] W. Zimmerschied, The Ohio State University, unpublished data.

TABLE I

PHYSICAL PROPERTIES AND ANALYSIS

| | Freezing range | F. p., °C. | B. p., °C. | $d^{20}_4$ | $n^{20}_D$ | *MR* | $AR_F$ | Chlorine % Calcd. | Chlorine % Found | Fluorine % Calcd. | Fluorine % Found |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $CH_3CF_2CH_2CH_3$ | 0.04 | −117.53 | 30.92 | 0.9159 | 1.3138 | 20.33 | 0.93 | | | | |
| $CH_3CF_2CH_2CH_2Cl$ | .01 | − 76.08 | 93.22 | 1.1552 | 1.3709 | 25.21 | .93 | 27.6 | 27.9 | 29.56 | 29.72 |
| $CH_2ClCF_2CH_2CH_3$ | .01 | − 78.96 | 82.72 | 1.1553 | 1.3685 | 25.08 | .88 | 27.6 | 27.7 | | |
| $CH_3CF_2CHClCH_3$ | .01 | − 92.1 | 72.32 | 1.1259 | 1.3631 | 25.16 | .91 | 27.6 | 28.0 | 29.56 | 29.89 |
| $CH_3CF_2CCl_2CH_3$ | .2 | + 43.66 | 89.84 | 1.2393 (at 50°) | 1.3752 (at 50°) | 30.12 | .96 | 43.5 | 43.2 | 23.31 | 23.01 |
| $CHCl_2CF_2CH_2CH_3$ | .1 | − 54.39 | 111.22 | 1.3113 | 1.3978 | 29.99 | .89 | 43.5 | 43.6 | | |
| $CH_3CF_2CH_2CHCl_2$ | .01 | − 66.90 | 119.26 | 1.3138 | 1.4017 | 30.19 | .99 | 43.5 | 43.3 | 23.31 | 22.80 |
| $CH_2ClCF_2CHClCH_3$ | 1.8 | − 60.5 | 115.67 | 1.3276 | 1.4025 | 29.93 | .86 | 43.5 | 43.6 | | |
| $CH_3CF_2CHClCH_2Cl$ | .. | ...... | 123.1 | 1.328 | 1.404 | 30.0 | .90 | 43.5 | 43.1 | | |
| $CH_2ClCF_2CH_2CH_2Cl$ | 0.5 | − 28.7 | 142.28 | 1.3652 | 1.4153 | 29.99 | .89 | 43.5 | 43.6 | | |
| $CH_3CF_2CH_2CCl_3$ | .9 | − 29.5 | 139.15 | 1.4366 | 1.4245 | 35.11 | 1.02 | 53.9 | 54.2 | | |
| $CH_3CF_2CHClCHCl_2$ | .. | ...... | 146 | .... | 1.431 | ... | .. | .. | .. | | |
| $CCl_3CF_2CCl_2CCl_3$ | .06 | − 8.42 | 98.2 mm. | 1.8990 | 1.5198 | 59.15 | 0.87 | | | [a] | |
| $CH_3CFClCH_2CH_3$ | .2 | −110.06 | 67.65 | 0.9982 | 1.3782 | 25.55 | 1.11 | 32.1 | 32.3 | 17.19 | 16.71 |
| $CH_3CF_2CH_2CF_3$ | .01 | − 35.01 | 40.14 | 1.2666 | 1.2824 | 20.67 | 1.10 | | | | |
| $CH_3CCl{=}CHCH_3$ *cis* isomer | .9 | −117.3 | 70.58 | 0.9239 | 1.4240 | 25.01 | | | | [b] | |
| $CH_3CCl{=}CHCH_3$ *trans* isomer | .8 | −105.8 | 62.84 | 0.9139 | 1.4190 | 25.02 | | | | | |
| $CH_2ClCCl_2CHClCH_3$ | 2.0 | − 46 to −48 | 182 | 1.426 | 1.491 | 39.7 | | | | | |
| $CHCl_2CCl_2CH_2CH_3$ | .. | Glass | 180 | 1.426 | 1.490 | 39.7 | | | | | |

[a] Improves data of Henne, Renoll and Leicester, THIS JOURNAL, **61**, 938 (1939). [b] Improves the literature data.

The interpretation was made that the $CF_2$ group immobilizes the chlorine atoms in alpha position, represses the reactivity of the chlorine atoms in beta position, and is practically without effect on the chlorine atoms in gamma position.

Dehydrohalogenation with boiling alcoholic potassium hydroxide does not take place at all with $CH_2ClCF_2CH_2CH_3$, nor $CH_3CF_2CHClCH_3$. The reaction, however, occurs very easily with $CH_3CF_2CH_2CH_2Cl$. This can be interpreted on the basis of the reactivity of the chlorine atoms, in the same fashion as the preceding test. Or else, if one considers that in dehydrohalogenation the controlling factor is the ability of a hydrogen to come off as a proton, then it can be reasoned that in pulling electrons toward itself, the $CF_2$ group loosens the binding of the alpha hydrogens, or, in other words, enhances their ability to be given off as a proton.

## Purification and Physical Constants

Chemical purification was used only on such derivatives which proved to be contaminated by olefinic impurities, because the boiling points of compounds of the $CRR'{=}CR''R'''$ and $CRR'H{-}CR''R'''F$ types are frequently very close together. A treatment with bromine or chlorine in sunlight was effective in these cases. This treatment eliminates the olefins, but also halogenates some material by substitution, hence causes appreciable losses when not well controlled.

Physical purification was accomplished by repeated distillation through an adiabatic column one meter long and 15 mm. in diameter, packed with glass helices, and fitted with a total reflux–partial take off head. Tested with toluene and methylcyclohexane, by the method of Fenske,[9] this column rated 19 plates.

The criterion of purity was, in all cases, the shape of the freezing curve or melting curve, determined on samples of about 50 g. with a resistance thermometer reading to 0.001°. The method of operation and of extrapolation of the freezing point to perfect purity was that of the Bureau of Standards.[10] The freezing range recorded in the table is that between incipient crystallization and inability further to stir the mass.

The normal boiling points were taken in a modified Cottrell apparatus[11] with a resistance thermometer and an automatic monostat to regulate the pressure at 760 mm.

The densities were taken with a Sprengel type pycnometer of 5-ml. capacity. Low boiling materials were measured in sealed pycnometers of the same capacity.

The refractive indices were measured with an Abbe refractometer. The molecular refraction was calculated by the Lorenz–Lorentz formula. Subtracting from the experimental values the customary increments for carbon (2.418), hydrogen (1.100), chlorine (5.967) and double bond (1.733) gave the listed value for $AR_F$, the atomic refraction of fluorine.

The analyses were performed on the micro scale by decomposition with heated potassium[12] or with sodium peroxide in a Monel bomb.[13]

## Summary

$CH_3CF_2CH_2CH_3$ was synthesized by interaction of dry hydrogen fluoride with commercial $CH_3CCl{=}CHCH_3$. Its chlorination gave only $CH_3CF_2CHClCH_3$(A) and $CH_3CF_2CH_2CH_2Cl$(B). On

---

(9) Fenske, *Ind. Eng. Chem.*, **24**, 482 (1932).

(10) Mair, Glasgow and Rossini, *J. Research Natl. Bur. Standards*, **26**, 591 (1941).

(11) Quiggle, Tongberg and Fenske, *Ind. Eng. Chem., Anal. Ed.*, **6**, 466 (1934).

(12) The Hoffman Microanalytical Laboratories, Denver, Colorado.

(13) J. Varner, Thesis, The Ohio State University, 1943.

further chlorination **A** gave only $CH_3CF_2CCl_2CH_3$ and $CH_3CF_2CHClCH_2Cl$, while **B** gave $CH_3CF_2CH_2CHCl_2$, then $CH_3CF_2CH_2CCl_3$ almost exclusively. These results show that the chlorination is directed away from an alpha $CH_3$ group, and tends to accumulate the chlorine atoms on the same carbon atoms. The failure of $CH_2ClCF_2CH_2CH_3$ to be chlorinated to $CHCl_2CF_2CH_2CH_3$ confirms the direction away from a terminal group alpha to a $CF_2$ group.

Chlorine reactivity tests show that alpha chlorine atoms are immobilized and that beta chlorine atoms are repressed, while gamma chlorine atoms seem to be unaffected.

COLUMBUS, OHIO RECEIVED MAY 7, 1945[14]

---

[14] This manuscript was originally received on September 24, 1943, and after examination by the editorial board was accepted for publication in THIS JOURNAL. It was, however, referred to the National Defense Research Committee and at their request was withheld from publication, in a confidential file, until clearance was granted on May 5, 1945.

---

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AT THE OHIO STATE UNIVERSITY]

# The Synthesis and Directed Chlorination of 1,1,1,-Trifluorobutane

BY ALBERT L. HENNE AND JAMES B. HINKAMP

To find out how far a $CF_3$ group would extend its influence, trifluorobutane, $CF_3CH_2CH_2CH_3$, was synthesized and subjected to the action of chlorine. The synthesis problem consisted in devising a practical method for obtaining an intermediate compound, $CCl_2{=}CHCH_2CH_3$, from which the desired $CF_3CH_2CH_2CH_3$ was made by variations of the procedures previously used to synthesize $CF_3CH_2CH_3$.[1] The chlorination as well as the isolation and identification of the chlorinated compounds were performed in a manner previously described.[1,2]

## Synthesis of $CCl_2{=}CHCH_2CH_3$

The sequence $CHOCH_2CH_2CH_3$, to $CHCl_2CH_2CH_2CH_3$, to $CHCl{=}CHCH_2CH_3$, to $CHCl_2CHClCH_2CH_3$, to $CCl_2{=}CHCH_2CH_3$, was first tried. The transformation of butyraldehyde into its dichloride by means of phosphorus pentachloride gave only a 23% yield, which was finally brought up to 39% by a series of time-consuming improvements. Since these improvements called for hydrolysis of the reaction product at 0°, the risk of handling an incompletely hydrolyzed material prevented their application to larger quantities. The dehydrohalogenation to $CHCl{=}CHCH_2CH_3$ required a saturated solution of potassium hydroxide in boiling butanol, and gave 64% of olefin together with 29% of recovered dichloride.

For large quantities it was deemed safer and more economical to start from technical $CH_2ClCHClCH_2CH_3$. Dehydrohalogenation occurred easily with a 30% solution of sodium hydroxide in denatured alcohol and formed only two of the possible three olefins. The reaction was sufficiently exothermic to maintain itself and it yielded 27% of $CH_2{=}CClCH_2CH_3$, 46% of the desired $CHCl{=}CHCH_2CH_3$ and 16% of recovered dichloride. Since $CH_2{=}CClCH_2CH_3$ was easily transformed into $CH_3CF_2CH_2CH_3$ used in the preceding study,[2] this procedure proved to be very satisfactory. The addition of chlorine which synthesizes $CHCl_2CHClCH_2CH_3$ was performed in the dark to prevent substitution. Pilot tests showed that water would greatly accelerate the rate of addition, but at the expense of increased substitution. When time matters little, it is best to operate without water, at about 10°, and with a slight excess of olefin, for a net yield of 70–75%. In the presence of water, the reaction proceeds nearly four times faster, but the net yield drops to approximately 55%.

The dehydrohalogenation of $CHCl_2CHClCH_2CH_3$ proceeded very easily with either aqueous or alcoholic sodium hydroxide, and gave 96% of the desired $CCl_2{=}CHCH_2CH_3$.

## Synthesis of $CF_3CH_2CH_2CH_3$

At room temperature, $CCl_2{=}CHCH_2CH_3$ does not react with hydrogen fluoride. When the temperature is raised, addition takes place to form $CFCl_2CH_2CH_2CH_3$, then substitution occurs to yield $CF_2ClCH_2CH_2CH_3$. With longer reaction periods, higher temperatures, and a greater excess of hydrogen fluoride, the formation of $CF_2ClCH_2CH_2CH_3$ is progressively enhanced.

A three mole quantity of $CCl_2{=}CHCH_2CH_3$ was mixed with 24 moles of hydrogen fluoride in a steel container surmounted by a one meter length of half-inch steel pipe bearing a pressure gage and a releasing needle valve. The top twenty centimeters of the pipe were surrounded by a jacket which could be filled with Dry Ice. The reaction was started by putting the cylinder in a hot water bath, its progress being shown by an increase in pressure due to the formation of hydrogen chloride. With Dry Ice in its container to ensure an efficient dephlegmation, the hydrogen chloride was slowly released into a water absorber by operating the needle valve so as to maintain the pressure between 17 and 20 atmospheres. When the pressure no longer increased, the reaction vessel was cooled in Dry Ice, and its contents were poured onto cracked ice, then worked up by

---

(1) Henne and Whaley, THIS JOURNAL, 64, 1157 (1942).

(2) Henne and Hinkamp, *ibid.*, 67, 1194 (1945).