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## Summary

Microscopic observations of appearance and optical properties of the polymorphs of some one-acid triglycerides have been used to supplement X-ray and melting point data. Further support has been given for the existence of but three polymorphic forms of tristearin, etc. In particular, the minimum-melting form (alpha) is *not* vitreous, but is much more highly ordered, probably a somewhat disordered crystal. It is believed that no vitreous form exists for these triglycerides.

The crystals of lowest interference color obtainable (between crossed nicols) have the intermediate melting point (65° for tristearin), rather than the minimum melting point; they give the beta prime X-ray pattern, not the alpha. By a suitable choice of crystallization temperature one can obtain better-organized, intermediate-melting crystals of high interference color; these also melt near 65° and show the beta prime X-ray pattern; in addition, single crystals show beta prime optical properties.

It is shown how the "seven" forms, described by Weygand and Grüntzig upon the basis of microscopic observations plus thermal data alone, are to be reduced to the three revealed by X-rays.

IVORYDALE 17, OHIO RECEIVED MAY 11, 1950

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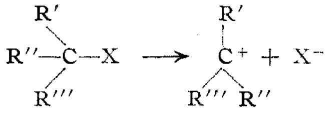
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PURDUE UNIVERSITY]

# Chemical Effects of Steric Strains. III. The Effect of the Halogen on the Rate of Hydrolysis of Tertiary Aliphatic Halides

BY HERBERT C. BROWN AND ANNETTE STERN

It has been proposed that three alkyl groups attached to a single carbon atom constitute a center of strain and that such strain may exert an important influence upon the chemistry of highly branched carbon compounds.[1] To test the value of this concept in interpreting the behavior of highly branched carbon compounds, we have undertaken quantitative studies of the effect of structure on the reactions of such compounds.

The hydrolysis of tertiary alphatic halides is believed to proceed through a rate determining ionization followed by a rapid reaction of the carbonium ion with the solvent.[2] The steric strain hypothesis proposes that the bulkier the groups, R′, R″, R‴, the greater the strain. Ionization to the presumably planar carbonium ion should diminish the strain. Therefore, other factors being maintained essentially constant, an increase in the steric requirements of the groups R should result in an increase in the rate of hydrolysis.

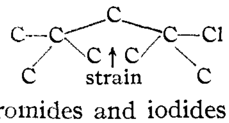


The first paper of this series[1] reported a study of the effect of structure on the rate of hydrolysis of twelve tertiary aliphatic chlorides. The results would be exceedingly difficult to interpret without the aid of the steric strain concept.

The present investigation was undertaken to determine whether the structural effects observed in the tertiary aliphatic chlorides are also present in the corresponding bromides and iodides. The recent publication of a paper reporting rate data for the hydrolysis of tertiary iodides[3] made it possible to restrict this study to the hydrolysis of tertiary bromides of the structure $RMe_2CBr$ (with R = Me, Et, *i*-Pr, *t*-Bu and *neo*-Am).

## Results and Discussion

In the alkyl chlorides the rate of hydrolysis first rises as R is changed from Me to Et, and then drops as R becomes isopropyl (Fig. 1). Because of the geometry of the ethyl and isopropyl groups which permits rotation of the groups to positions minimizing the crowding, the strain in the alkyl chloride should not be appreciably increased in this sequence of structural changes. The observed changes in rate can be attributed to the combined inductive and hyperconjugative effects of the alkyl groups.[1] However, on this basis triptyl chloride (R = *t*-Bu) should show a further drop in rate. Instead an increase is observed. This increase is attributed to steric strain. Diisobutylene hydrochloride (R = *neo*-Am) shows a large increase in rate of hydrolysis and the geometry of the molecule is such as to lead to a large increase in steric strain.



The alkyl bromides and iodides show identical changes in the rates of hydrolysis as R is suc-

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[1] Brown and Fletcher, THIS JOURNAL, **71**, 1845 (1949).

[2] The evidence is summarized in papers by Hughes, *Trans. Faraday Soc.*, **37**, 603 (1941), and *J. Chem. Soc.*, 968 (1946).

[3] Shorter and Hinshelwood, *J. Chem. Soc.*, 2412 (1949).

TABLE I

RATE OF HYDROLYSIS OF TERTIARY ALIPHATIC HALIDES IN "80%" AQUEOUS ETHANOL AT 25°

| Alkyl halides, $RMe_2CX$ | R | $k_1 \times 10^5$ sec. | | | $r_1$[a] | | | $r_2$[b] | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | Cl[c] | Br[d] | I[e] | Cl | Br | I | Cl | Br | I |
| *t*-Butyl | Me | 0.92 | 35.8[f] | 92.6 | 1.00 | 38.9 | 100 | 1.00 | 1.00 | 1.00 |
| *t*-Amyl | Et | 1.53 | 63.6[f] | 188.5 | 1.00 | 41.6 | 123 | 1.66 | 1.78 | 2.04 |
| Dimethylisopropylcarbinyl | *i*-Pr | 0.81 | 43.5 | 149.5 | 1.00 | 53.7 | 184 | 0.88 | 1.22 | 1.61 |
| Dimethyl-*t*-butylcarbinyl | *t*-Bu | 1.11 | 60.0 | 263 | 1.00 | 54.1 | 237 | 1.21 | 1.68 | 2.84 |
| Dimethylneopentylcarbinyl | *neo*-$C_5$ | 20.6 | (1300)[g] | | 1.00 | 63.1 | | 22.4 | 36.3 | |

[a] $r_1 = k_1(RMe_2X)/k_1(RMe_2CCl)$. [b] $r_2 = k_1(RMeCX)/k_1(Me_3CX)$. [c] Data from ref. 1. Density of solvent is $d^{25}{}_4$ 0.8496. [d] Data from present investigation. Density of solvent is $d^{25}{}_4$ 0.8494. In this solvent $k_1$ for *t*-butyl chloride is $0.90 \times 10^{-5}$ sec.$^{-1}$. [e] Data from ref. 2. Solvent not characterized other than as approximately "80%" aqueous ethanol by volume. [f] Cooper and Hughes, *J. Chem. Soc.*, 1184 (1937), report for *t*-butyl bromide $k_1 = 37.4 \times 10^{-5}$ sec.$^{-1}$ at 25° in 80% ethanol. Hughes and McNulty, *ibid.*, p. 1285, report for *t*-amyl bromide $k_1 = 58.3 \times 10^{-5}$ sec.$^{-1}$ at 25.2°. The first value is in fair agreement with our constant; the second is several per cent. lower. Unfortunately, there is no indication that the same solvent was used in both rate constant measurements and the composition of the solvent is not specified other than as "80%" by volume. [g] Rate was measured in "90%" aqueous ethanol. The value for "80%" ethanol given in Table I was estimated from the relative values of $k_1$ for *t*-butyl and *t*-amyl bromides in the two solvents. In "90%" ethanol ($d^{25}{}_4$ 0.8173) the values of $k_1$ ($10^{-5}$ sec.$^{-1}$) are *t*-butyl bromide, 5.30; *t*-amyl bromide, 11.4; dimethylneopentylcarbinyl bromide, 208.

cessively altered from Me to Et to *i*-Pr to *t*-Bu (Table I, Fig. 1). Therefore, the factors, both polar and steric, which are at the basis of the observed changes in the alkyl chlorides persist in the corresponding bromides and iodides.

In confirmation of general experience the tertiary bromides and iodides hydrolyze much more rapidly than the chlorides. Thus, *t*-butyl iodide hydrolyzes at a rate 100 times greater than *t*-butyl chloride and dimethyl-*t*-butylcarbinyl iodide at a rate 237 times greater than the corresponding chloride. Although steric strain probably plays a part in this increased rate, it is highly likely that the more important factor here is the decreased strengths of the carbon–bromine and carbon–iodine bonds relative to the carbon–chlorine bond. Alkyl bromides and iodides are more reactive than chlorides in bimolecular displacement reactions for much the same reason.

It was previously suggested that steric strain is a factor in the ionization of tertiary aliphatic chlorides. As the halogen is altered from chlorine to bromine to iodine, the increasing bulk of the halogen should lead to increasing steric strains in the alkyl halide and result in an increasing tendency for the alkyl halide to undergo ionization. Unfortunately, direct observation of this effect is rendered difficult by the very large increase in rate accompanying the decrease in carbon–halogen bond strength. Fortunately, it is possible to obtain evidence as to the importance of steric effects by handling the data so as largely to eliminate the effect of the change in bond strength resulting from the change in the polar characteristics of the halogen. In the absence of steric effects one would expect the ratio

$$r_1 = k_1(RMe_2CX)/k_1(RMe_2CCl)$$

either to remain sensibly constant as R successively becomes Me, Et, *i*-Pr, *t*-Bu, or at most to show minor variations in accordance with the changes in the rate constant $k_1$. However, if steric effects are important in the tertiary chlorides, $RMe_2CCl$, they should become even greater in the corresponding bromides and iodides. The effect should be magnified by increasing steric requirements of the alkyl group R. It is therefore significant that the quantity $r$ is not sensibly constant (Table I), but increases regularly with increasing steric requirements both of the halogen (iodine > bromine > chlorine) and of the alkyl group (*neo*-Am > *t*-Bu > *i*-Pr > Et > Me).

Comparison of the rates of hydrolysis of a given halide, $RMe_2CX$, with the corresponding tertiary butyl halide, $Me_3CX$, points to the same conclusion. The ratio of the two rates

$$r_2 = k_1(RMe_2CX)/k_1(Me_3CX)$$

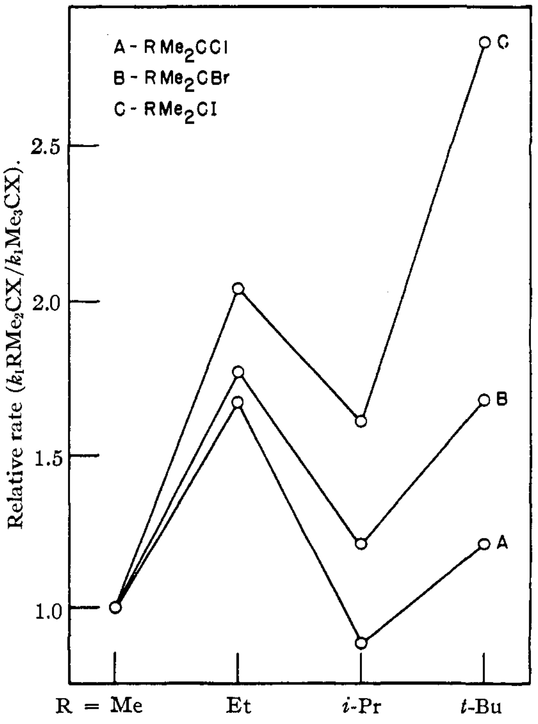

Fig. 1.—Relative rates of hydrolysis of tertiary halides, $RMe_2CX$.

increases from 1.66 for chlorine, to 1.78 for bromine, to 2.04 for iodine, in the case of the *t*-amyl halides. The quantity $r_2$ shows an even greater increase with the dimethylisopropyl- and the dimethyl-*t*-butylcarbinyl halides (Table I, Fig. 1).

This parallelism between the predicted increase in steric strain and the observed increase in relative rates of hydrolysis strongly supports the conclusion that such strains must be an important factor in the unimolecular hydrolysis of tertiary halides and must play a part in the increased rates of hydrolysis of tertiary bromides and iodides.

Shorter and Hinshelwood[3] have interpreted their results on a somewhat different basis than that which we have advanced. For example, they consider steric effects only from the classical viewpoint of hindrance of reaction velocity and fail to consider the effects of steric crowding in facilitating the ionization stage. Much of their discussion is based on the marked differences in the non-exponential factor of the Arrhenius equation ($k = Ae^{-E/RT}$) which they calculate for alkyl chlorides and alkyl iodides ($A \times 10^{-10}$ for *t*-butyl chloride is 10.5; iodide, 1740). However, these marked differences in the *A*-factor result from unusually low activation energies which they obtain for the hydrolysis of tertiary alkyl chlorides. For example, their value, 21.70 kcal. for *t*-butyl chloride, is in marked disagreement with the value 23.06 kcal. for this compound obtained by Hughes.[4] Results obtained in our own investigations[5] agree closely with the values reported by Hughes and differ from those of Shorter and Hinshelwood. If the higher values for the activation energies are used, the marked difference in the *A*-factors for the tertiary chlorides and iodides disappears. For that reason it appears desirable to defer discussion of the treatment by Shorter and Hinshelwood until their unusual activation energy values can be verified.

## Experimental Part

*t*-Butyl and *t*-amyl bromides were prepared by treating the commercial alcohols (redistilled) with hydrogen bromide. Dimethylisopropylcarbinol was prepared by treating ethyl isobutyrate with two moles of methylmagnesium iodide and converted to the bromide with hydrogen bromide. Dimethyl-*t*-butylcarbinyl bromide was a sample prepared by the bromination of triptane.[6] Diisobutylene hydrobromide was prepared by addition of hydrogen bromide to diisobutylene. The liquid tertiary bromides were distilled through a Vigreux column and middle fractions utilized for the rate studies. Physical constants are summarized in Table II.

TABLE II

PHYSICAL CONSTANTS OF TERTIARY BROMIDES

| Tertiary bromide | B. p., °C. | Pressure, mm. | $n^{20}D$ |
|---|---|---|---|
| *t*-Butyl | 70–71 | 742 | 1.4344 |
| *t*-Amyl | 103.5–104 | 744 | 1.4421 |
| Dimethylisopropylcarbinyl | 58–59 | 71 | 1.4516 |
| Dimethyl-*t*-butylcarbinyl | M. p. 150–152 | | |
| Dimethylneopentylcarbinyl | 62–63 | 18 | 1.4557 |

The experimental procedure used in this investigation is described in the first paper of this series.[1] The results of a typical rate study is presented in Table III.

TABLE III

RATE DATA FOR THE HYDROLYSIS OF DIMETHYLISOPROPYLCARBINYL BROMIDE

| Time, sec. | $x$ ml., NaOH | $k_1 \times 10^5$ sec. |
|---|---|---|
| 0 | 0 | |
| 300 | 0.92 | 43.6 |
| 600 | 1.65 | 43.4 |
| 900 | 2.39 | 43.8 |
| 1200 | 3.01 | 44.0 |
| 1800 | 3.98 | 43.4 |
| 2700 | 5.20 | 45.5 |
| ∞ | $7.34 = a$ | |
| | Average $k_1$ | $43.8 \times 10^{-5}$ sec.$^{-1}$ |

At least four separate rate studies were made for each alkyl halide. Thus, for dimethyl-*t*-butylcarbinyl bromide, values of $k_1$ of 60.9, 59.8, 59.4, 60.0 ($10^{-5}$ sec.$^{-1}$) illustrate the precision attained. The average value of these four determinations, $60.0 \times 10^{-5}$ sec.$^{-1}$, is listed in Table I.

## Summary

The rate constants for the first order hydrolysis of a series of tertiary bromides $RMe_2CBr$ in 80% aqueous ethanol have been determined. The rate constants change with the group R (Me, Et, *i*-Pr, *t*-Bu, and *neo*-Am) in the tertiary bromides in a manner similar to that previously observed in the corresponding chlorides and iodides. The rate constant ratios, $r_1 = k_1(RMe_2CX)/k_1(RMe_2CCl)$ and $r_2 = k_1(RMe_2CX)/k_1(Me_3CX)$ increase from the chlorides to the bromides to the iodides in such a manner as to point to an increase of steric strain with increase in the bulk of the halogen as well as with increase in the bulk of the alkyl group. The effect of structure upon the rate of hydrolysis of tertiary alkyl halides is explicable in terms of the steric strain hypothesis presented previously.

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[4] Hughes, *J. Chem. Soc.*, 255 (1935).

[5] Unpublished studies with Dr. Hans Berneis and Mr. M. Borkowski.

[6] Unpublished work with Mr. Glen A. Russell.