the higher rate of the exchange in liquid sulfuric acid is not yet entirely apparent.

Speculation on the mechanism of the reaction is tempting, but this must await a more detailed kinetic study; it is planned that such will be undertaken in the near future.

Acknowledgment.—This work was supported by a grant-in-aid from General Research funds administered by the Graduate Council of Oregon State College, for which the author wishes to express his appreciation.

Summary

Using radioactive S^{35} the exchange reaction between sulfur dioxide and sulfuric acid (97.2%) has been investigated over the range from room temperature to 211°. The observed half-times for exchange are: at room temperature, > 27 yr.; at 101°, ~1.6 yr.; at 211°, ~7.5 hr. The temperature coefficient of the rate is, at 165°, ~1.8 per 10°, corresponding to an apparent activation energy of 22.0 kcal./mole.

CORVALLIS, OREGON RECEIVED AUGUST 23, 1949

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF WAYNE UNIVERSITY]

Chemical Effects of Steric Strains. II. The Effect of Structure on Olefin Formation in the Hydrolysis of Tertiary Aliphatic Chlorides

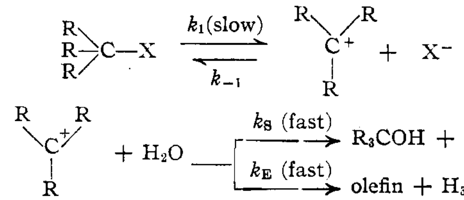
BY HERBERT C. BROWN[1] AND ROSLYN SILBER FLETCHER[1,2]

It has been suggested that the accumulation of three or four alkyl groups on a single carbon atom may constitute a center of strain and that such strain (B-strain) could be an important factor in the reactions of highly branched carbon compounds.[3] To test this hypothesis, a study was made of the rates of hydrolysis of twelve tertiary aliphatic chlorides in 80% aqueous alcohol.[4] The effect of structure on the rates of hydrolysis would be difficult to understand without the assistance of the B-strain concept. The present investigation was undertaken to learn whether the steric strain concept could contribute to an understanding of the effect of structure on olefin formation in the hydrolysis of tertiary chlorides.

The topic of elimination reactions has recently been the subject of an extensive discussion by Hughes and Ingold.[5] These authors conclude that steric effects are "seldom important in unimolecular reactions" and the dominating factor in unimolecular eliminations involves electromeric effects. Unfortunately, Hughes and Ingold base their conclusions on the study of eliminations involving but two different tertiary alkyl radicals, *t*-butyl and *t*-amyl. The present study of structural effects of some twelve different tertiary alkyl radicals permits a more detailed analysis of influence of structure on the course of the elimination reaction.

Results

Hughes and Ingold have offered convincing evidence that the hydrolysis of tertiary chlorides in aqueous solvents proceeds through the mechanism[6]



$$R_3C{-}X \underset{k_{-1}}{\overset{k_1(\text{slow})}{\rightleftharpoons}} R_3C^+ + X^-$$

$$R_3C^+ + H_2O \begin{cases} \xrightarrow{k_S\ (\text{fast})} R_3COH + H^+ \\ \xrightarrow{k_E\ (\text{fast})} \text{olefin} + H_3O^+ \end{cases}$$

Therefore, determination of the quantity of olefin and of hydrogen ion formed in a given period of time yields the fraction of olefin present in the product. This quantity is identical with the ratio $k_E/(k_E + k_S)$, where k_E is the unknown rate constant for the elimination reaction and k_S is the unknown rate constant for the substitution reaction. The results are summarized in Table I.

TABLE I

OLEFIN FORMATION IN THE HYDROLYSIS OF TERTIARY ALKYL CHLORIDES AT 25° IN "80%" AQUEOUS ETHANOL[a]

	Alkyl chloride, R'R''R'''CCl	R'	R''	R'''	$k_E/(k_E + k_S)$
1	*t*-Butyl[b]	Me	Me	Me	0.16
2	*t*-Amyl[c]	Me	Me	Et	.34
3	Dimethyl-*n*-propylcarbinyl	Me	Me	*n*-Pr	.33
4	Dimethylisopropylcarbinyl	Me	Me	*i*-Pr	.62
5	Dimethyl-*n*-butylcarbinyl	Me	Me	*n*-Bu	.35
6	Dimethyl-*t*-butylcarbinyl	Me	Me	*t*-Bu	.61
7	Dimethylneopentylcarbinyl	Me	Me	neo-C_5	.65
8	Methyldiethylcarbinyl	Me	Et	Et	.41
9	Triethylcarbinyl	Et	Et	Et	.40
10	Diethylisopropylcarbinyl	Et	Et	*i*-Pr	.80
11	Diethyl-*t*-butylcarbinyl	Et	Et	*t*-Bu	.90
12	Methyldiisopropylcarbinyl	Me	*i*-Pr	*i*-Pr	.78

[a] Density d^{25}_4 0.8496. [b] Cooper, Hughes and Ingold, *J. Chem. Soc.*, 1280 (1937), report 17% olefin. [c] Hughes and McNulty, *ibid.*, 1283 (1937), report 33% olefin.

Discussion

The Steric Factor in the Elimination Reaction.

—According to the steric strain hypothesis, an increase in the size and bulk of the three alkyl groups, R, of a tertiary halide, R_3CX, should result in an increase in the strain at the tertiary carbon atom. Since such strain would be mark-

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[3] Brown, *Science*, **103**, 385 (1946).

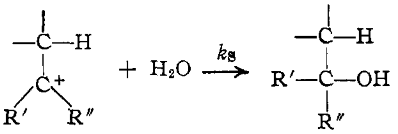
[4] Brown and Fletcher, THIS JOURNAL, **71**, 1845 (1949).

[5] Hughes, Ingold, *et al.*, *J. Chem. Soc.*, 2038–2119 (1948).

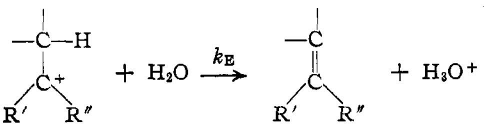
[6] Hughes and Ingold, *Trans. Faraday Soc.*, **37**, 657 (1941).

edly reduced in the presumably planar carbonium ion, such strain should facilitate ionization, the slow stage of the reaction. Although interpretation of the results is complicated by the need to consider the inductive and hyperconjugative effects of alkyl groups, the results[4] indicate a marked tendency for the rate of hydrolysis to increase with increasing steric requirements of the alkyl group, R.

Increase in the steric requirements of the three alkyl groups, R, should also affect the reactions of the carbonium ions formed by ionization of the halide, R_3CX. Just as steric strain is predicted to favor formation of the carbonium ion, steric strain would be expected to decrease the tendency for the ion to unite with a solvent molecule, thereby reforming a highly branched molecule with the original high strain. Therefore, increase in steric strain should decrease the magnitude of the rate constant for the substitution reaction, k_S.



At the same time, such residual strain as may remain in the carbonium ion after ionization should favor the loss of a proton from the alpha position. The effect would be expected to be quite small and much less important than the effect of steric strain on k_S. However, if the alpha hydrogen is itself located at a position of marked strain, its transfer to the solvent (or other base) should be particularly facile. In this case there should be observed a marked increase in the rate constant for the elimination reaction, k_E.



Since the rate constants k_S and k_E cannot be determined individually, it is necessary to deal with the olefin fraction, $k_E/(k_E + k_S)$.[5]

A decrease in k_S or an increase in k_E (or both) should increase the value of the fraction, $k_E/(k_E + k_S)$, and thereby result in an observed increase in the olefin content of the product. Accordingly, if steric strain is a factor, *increasing steric requirements of the three alkyl groups in the tertiary chloride should result in an increase in the olefin content of the product*, regardless of whether the effect is transmitted primarily through k_S or through k_E.

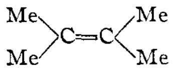
Electrometric Effects in the Elimination Reaction.[5]—The hydrolysis of *t*-amyl halides proceeds considerably faster than *t*-butyl halides. Moreover, the product from the former contains more olefin than that from the latter (Table I). Hughes and Ingold observed that the olefin formed from *t*-amyl is chiefly trimethylethylene, rather than 2-methyl-1-butene. From these and other observations they conclude that the unimolecular elimination reaction is controlled by electromeric effects and the reaction will proceed to the predominant formation of that olefin which is most stabilized by hyperconjugation. They further propose that the stabler the olefin formed, the greater should be the tendency toward the elimination reaction. In this way they explain the observation that *t*-amyl, which forms the relatively stable olefin, trimethylethylene, yields 34% olefin, while under identical conditions *t*-butyl, which forms the less stable olefin, isobutylene, produces but 16% olefin (Table I).

The Effect of Structure on the Elimination Reaction.—It is instructive to examine the experimental results (Table I) from these two different points of view, electromeric and steric.

Lengthening of the alkyl groups R in the series, RMe_2CCl, beyond two carbon atoms does not have any noticeable effect. Thus, the olefin fractions for the three chlorides of this series, R = Et, *n*-Pr, *n*-Bu, are 0.34, 0.33 and 0.35, respectively. Mere lengthening of the carbon chain should not be expected to affect the strain at the central carbon atom, so that the results are in accord with the steric strain hypothesis. Moreover, the olefins formed from these halides should be about equally stabilized by hyperconjugation, so that the results are equally in accord with this interpretation.

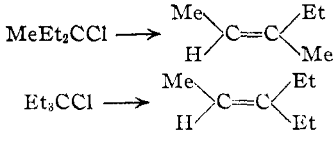
The increase in olefin fraction observed in going from Me_3CCl to $EtMe_2CCl$ can be attributed to electromeric effects, such as those proposed by Hughes and Ingold. Because of the geometry of the ethyl group, the replacement of the one methyl group in *t*-butyl chloride by the ethyl group in *t*-amyl chloride would not be expected to alter significantly the strain at the central carbon atom.

The large increase in olefin formation observed in dimethylisopropylcarbinyl chloride (0.62 as compared to 0.16 for *t*-butyl chloride) can be attributed either to the stability of the olefin which is probably the major product



or to the strain at the tertiary hydrogen, strain which is relieved by loss of the proton, or to both.

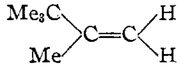
The increase in olefin fraction with increase in number of ethyl groups (Me_2EtCCl, 0.34; $MeEt_2CCl$, 0.41; Et_3CCl, 0.40) does not appear to be explicable in terms of the electromeric effect. An ethyl group, with two alpha hydrogen atoms, would be expected to stabilize an olefin through hyperconjugation less than a methyl group.

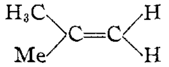


The observed change in olefin fraction can be attributed to combined electromeric and steric effects which operate in opposing directions.

The results obtained with dimethyl-*t*-butylcarbinyl chloride and dimethylneopentylcarbinyl chloride strongly indicate the need to consider steric strain effects in these reactions.

The olefin formed from dimethyl-*t*-butylcarbinyl chloride (A) would be expected to be somewhat less stable than that from *t*-butyl chloride (B). This conclusion is based on the decrease in hyperconjugation as the alpha hydrogen atoms are replaced by methyl groups.

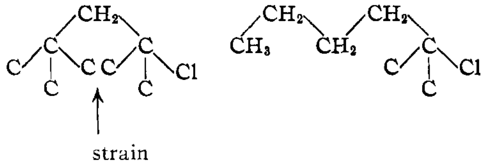
A


B


The treatment advanced by Hughes and Ingold would therefore predict that the unimolecular solvolysis of dimethyl-*t*-butylcarbinyl chloride would occur at a slower rate than *t*-butyl chloride, and the olefin fraction would be somewhat less than two-thirds that obtained from *t*-butyl chloride. However, dimethyl-*t*-butylcarbinyl chloride undergoes solvolysis somewhat more rapidly than *t*-butyl chloride.[4] Moreover, there is obtained an olefin fraction of 0.61, a value some six-fold that predicted.

It is proposed that the large increase in the olefin fraction is primarily a steric effect. The *t*-butyl group differs from the ethyl and isopropyl groups previously discussed in two respects. First, the *t*-butyl group has no hydrogen in a position suitable for participation in the elimination reaction. Second, the geometry of the group is such that steric strain in the molecule, dimethyl-*t*-butylcarbinyl chloride, cannot be relieved by rotation of the alkyl group as in the monoethyl and monoisopropyl analogs. Accordingly, the replacement of a methyl group in *t*-butyl chloride by a *t*-butyl group should lead to a considerable increase in steric strain. The carbonium ion is believed to be relatively strain-free. Addition of a solvent molecule would regenerate a strained molecule. The carbonium ion, therefore, largely reacts by the alternative path involving loss of a proton. If this interpretation is correct, the increase in olefin fraction in this case is brought about primarily by a decrease in k_S, although a minor increase in k_E is not excluded.

The validity of this interpretation is supported by the large olefin fraction, 0.65, observed for dimethylneopentylcarbinyl chloride. This chloride may be considered derived from *t*-butyl chloride by replacement of one of the alpha hydrogen atoms by a *t*-butyl group. It was previously noted that the introduction of a methyl, an ethyl, or a *n*-propyl group in this position ($R-CH_2CMe_2Cl$ with R = Me, Et, *n*-Pr) causes the resulting molecule to yield olefin fractions which are practically identical, within the limits 0.33–0.35. On the other hand, the similar substitution in this position of a tertiary butyl group ($t-Bu-CH_2CMe_2Cl$) causes a very sharp increase in the olefin fraction. Certainly an alkyl group in the position beta to the reaction center could hardly be expected to exert a polar effect sufficiently important as to influence the course of the reaction to the extent observed. However, as was pointed out previously,[4] the geometry of the molecule is such that the *t*-butyl group in the beta position must bring about a strained condition, whereas less bulky, more flexible substituents can avoid such strain.



As the number of bulky substituents is increased, there is an increasing tendency for the olefin fraction to increase toward the theoretical limit, 1.00 (Table I).

It is concluded that steric effects, in addition to hyperconjugative effects, must be considered in a complete theory of the effects of structure on the unimolecular elimination reactions of tertiary alkyl groups.

Experimental Part

Materials.—Preparation and properties of the tertiary chlorides are reported in an earlier publication.[4] All other chemicals were standard laboratory reagents of the highest purity available commercially.

Olefin Determinations.—The procedure used for the determination of the olefin fractions is a modification of that used by Hughes and McNulty.[7] In a round-bottomed long-necked flask was placed 100 ml. of the "80%" ethanol solvent. The flask was immersed in a constant temperature bath maintained at 25.0 ± 0.03°. When temperature equilibrium had been attained, approximately 1 ml. of the tertiary chloride was added to the flask and the contents were rapidly mixed by swirling.

At definite time intervals, two 5-ml. aliquots of the solution were pipetted out. One aliquot was added to 100 ml. of absolute alcohol at 0° (to stop the reaction) and the hydrochloric acid formed was determined by titration with standard alkali with methyl red as indicator.

The other aliquot was added to 100 ml. of carbon tetrachloride at 0°. The flasks, glass-stoppered, were covered with black cloth to prevent exposure to light. A known volume of a standard solution of bromine in carbon tetrachloride (approximately 0.02 *N*) was then added and allowed to react with the olefin for 0.5 hr., while the flask was maintained dark and at 0°. An excess of potassium iodide solution, usually 1.0 ml. of 3 *M* solution, was then added and allowed to react with the free bromine for 0.25 hr., while maintaining the temperature at 0° and excluding light. The iodine liberated was then titrated with standard sodium thiosulfate solution, approximately 0.02 *N*.

The fraction of carbonium ions undergoing the elimination reaction was calculated with the aid of the equation

$$\frac{k_E}{k_E + k_S} = \frac{b - y}{2x}\,\frac{N''}{N'}$$

The quantities *b* and *y* represent the number of ml. of sodium thiosulfate solution used to titrate a known volume of a standard solution of bromine in carbon tetrachloride and that required for the same volume of bromine solution

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[7] Hughes and McNulty, *J. Chem. Soc.* 1283 (1937).

after reaction with the 5-ml. olefin sample removed at the time t. The symbol N' refers to the normality of the sodium hydroxide solution and N'' refers to the normality of the sodium thiosulfate solution. The quantity $(b - y)N''/2$ gives the concentration of olefin at time t. Similarly, x is the concentration of alkyl halide hydrolyzed at time t in terms of the sodium hydroxide solution, and xN' gives the concentration of alkyl chloride hydrolyzed at time t. The ratio of these two quantities gives the olefin fraction, $k_E/(k_E + k_S)$, the fraction of the carbonium ions reacting by elimination.

The experimental procedure was tested with a number of olefins. The simpler olefins yielded results with an accuracy of ±1%. The more highly branched olefins were more difficult. In these cases it was necessary to standardize carefully both the time the bromine was in contact with the olefin and the excess of bromine used. Adoption of the procedure outlined permitted the standard solutions of olefins to be determined with an accuracy of better than ±3%. Accordingly, it is believed that the olefin fractions reported are accurate to at least this figure. The results of a typical determination, with abbreviated data, are reported in Table II.

TABLE II

DETERMINATION OF OLEFIN FRACTION IN HYDROLYSIS OF DIMETHYL-*t*-BUTYLCARBINYL CHLORIDE IN "80%" ETHANOL AT 25°: $N' = 0.03530$; $N'' = 0.01997$

t, hr.	x, ml.	k_1, hr.$^{-1}$	$b - y$, ml.	$k_E/(k_E + k_S)$
0	0		0	
3	0.96	0.0394	2.09	0.615
5	1.54	.0394	3.36	.616
7	2.07	.0392	4.61	.629
∞	8.62			

Summary

The quantity of olefin formed in the hydrolysis of twelve tertiary chlorides has been determined. The results indicate the importance of steric effects in unimolecular elimination reactions.

LAFAYETTE, IND. RECEIVED APRIL 30, 1949

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, UNIVERSITY OF PENNSYLVANIA]

A Study of the Polymerization of α- and β-Pinene with Friedel–Crafts Type Catalysts

BY WILLIAM J. ROBERTS[1] AND ALLAN R. DAY

The catalytic polymerization of the isomeric pinene constituents of turpentine has been the subject of a number of investigations.[2] Until recently, most of the published work has dealt with α-pinene. Burroughs[3] first clearly differentiated between the two pinenes, with respect to polymerization behavior. He reported that β-pinene, under the influence of aluminum chloride, gives a much higher yield of solid polymer. Furthermore, the latter has a higher melting point than the polymer from α-pinene.

In view of the lack of directly comparable polymerization data for the two pinenes, as well as the inconclusive and incomplete information bearing on the nature of the polymerization mechanisms and polymer structures, further investigation seemed advisable.

The catalytic conversion of α- and β-pinenes to polymers, which are non-volatile in superheated steam, was studied with a number of Friedel–Crafts catalysts. The temperature and concentrations were kept constant for this series of experiments. The results of this series of tests, Table I, show that the relative order of efficiencies of the catalysts used is about the same for both isomers. β-Pinene polymerizes very rapidly and with extreme exothermic vigor after less than 1% of aluminum chloride has been added. The polymerization of α-pinene, although highly exothermic, is noticeably less violent.

TABLE I

PINENE POLYMERIZATION TESTS. COMPARATIVE CATALYST EFFICIENCIES UNDER STANDARD CONDITIONS[a]

	α-Pinene		β-Pinene	
Catalyst	% Solid polymer	S. P. °C.[b]	% Solid polymer	S. P., °C.[b]
$AlBr_3$	35.3	85.0	93.2	136
$AlCl_3$	35.2	84.0	94.2	134
$ZrCl_4$	20.0	91.3	96.0	132
$AlCl_3 \cdot (C_2H_5)_2O$	18.0	67.3	76.5	102
BF_3[c]	14.2	67.0	54.0	104
$BF_3 \cdot (C_2H_5)_2O$	11.8	Semi-solid	43.0	68.0
$SnCl_4$	4.7	..	21.3	...
$BiCl_3$	0.1	..	5.6	...
$SbCl_3$	0.2	..	0.7	...
$ZnCl_2$	0.0	..	0.5	...

[a] Concentration of pinene, 50% in toluene; temperature 40–45°; amount of catalyst 5% (based on pinene); average molecular weight of α-pinene polymer 650, average molecular weight of β-pinene polymer 1500. [b] A. S. T. M. Ball and Ring Method D 36–26. [c] Gaseous boron trifluoride passed into the solution until the latter was saturated.

Figures 1, 2 and 3 show the effect of monomer concentration and temperature on solid polymer formation from the two pinenes. The pinenes differ markedly in response to decreasing temperature of polymerization.[3] In general, maximum solid polymer yields were obtained from β-pinene at −30° and from α-pinene at 40°.

The variation in softening point with molecular weight for polymers from α-pinene, β-pinene and

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[2] Frankforter and Poppe, Orig. Com. 8th Intern. Congr. Appl. Chem. (appendix), **25**, 363 (1912); Steinkopf and Freund, *Ber.*, **47**, 411 (1914); Waterman, Leendertse and Koelensmid, *Rec. trav. chim.*, **55**, 7 (1936); Kondakow and Saprikin, *Bull. soc. chim.*, **37**, 1045 (1925); Thomas, U. S. Patent 1,939,932, Dec. 19. 1933; Carmody and Carmody, THIS JOURNAL, **59**, 1312 (1937).

[3] U. S. Patent 2,335,912, Dec. 7, 1943; see also Borglin, U. S. Patent 2,405,558, Aug. 13 ,1946.