occur in benzene at 193, 195, 201 and 204 mμ[29] (as is the case in dimethylaniline[30]).

Consequently the second primary band would correspond to the 183 mμ transition in benzene.[31]

The behavior of the absorption bands permits the conclusion that the first primary bands in the halonitrobenzenes (around 260 mμ) are charac-

(29) J. R. Platt and H. B. Klevens, *Chem. Revs.*, **41**, 301 (1947).

(30) H. B. Klevens and J. R. Platt, THIS JOURNAL, **71**, 1714 (1949).

(31) The assignment can be made with certainty only when measurements in the vacuum ultraviolet are available.

teristic for transitions in which ionic resonance forms with coplanar arrangement of nitro group and nucleus contribute largely to the excited states. This is evidently not the case for the secondary and first primary bands which appear independent of steric effects.[32]

(32) NOTE ADDED IN PROOF.—Since the acceptance of this paper the absorption spectra of the iodonitrobenzenes have been described by J. Ferguson and T. Iredale [*J. Chem. Soc.*, 2959 (1953)] and those of the fluoronitrobenzenes by W. Gruber [*Can. J. Chem.*, **31**, 1020 (1953)]. Their results are qualitatively in agreement with those reported here.

LAS VEGAS, NEW MEXICO

The Effects of Deuterium Substitution on the Rates of Organic Reactions. III.[1,2] Solvolysis Rates and Arrhenius Parameters for 2,3-Dimethyl-2-chlorobutane and its 3-Deutero Analog

BY V. J. SHINER, JR.

The observations of the effect of the β-deuterium substitution on the solvolysis rates of tertiary alkyl chlorides have been extended to include the case of a tertiary deuterium atom. The solvolysis rate constants in 80% aqueous alcohol at 25° for 2,3-dimethyl-2-chlorobutane and its 3-deutero analog are 8.68 and 6.76 × 10^{-6} sec.$^{-1}$, respectively. The deuterium compound has an activation energy 580 ± 70 calories higher and a log frequency factor 0.32 ± 0.03 unit higher than the hydrogen compound. The order of the isotope rate effect in the series $-CD_3$, $-CD_2-$, $-CD-$ and the hypothesis of elimination type driving forces suggests a reinterpretation of the effect of β-branching on solvolysis rates which does not involve two conflicting electronic influences. Similarly suggested is a possible reinterpretation of the polar effects of alkyl groups in ionic reactions, customarily explained by hyperconjugation.

In part II[2] which initiated the study of the effect of deuterium substitution on the rates of the S_N1-E1 solvolysis reactions of tertiary alkyl compounds, the effect of deuterium substitution for primary and secondary hydrogens adjacent to the reaction center was reported. In this paper the observations are extended to include the effects of deuterium substitution for an adjacent tertiary hydrogen atom. This example also has been used to analyze the effect of β-deuterium substitution in terms of the parameters in the Arrhenius equation. In the previous paper it was assumed that the most important effect was the change in the activation energy and for this case the validity of this assumption is tested.

$$(CH_3)_2—CH—C(CH_3)_2—Cl \quad (CH_3)_2—CD—C(CH_3)_2—Cl$$

$$\text{I} \qquad\qquad\qquad\qquad \text{II}$$
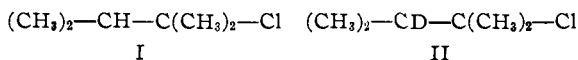
Compound I was prepared in the conventional manner by treatment of dimethylisopropylcarbinol with concentrated hydrochloric acid. The deuterium analog II was prepared by the addition of deuterium chloride to tetramethylethylene. This was accomplished by the slow addition of deuterium oxide[3] to a stirred solution of tetramethylethylene in excess acetyl chloride.[4]

The solvolysis reactions were followed by the titration of developed acid in aliquots taken at suitable time intervals to more than 75% completion. The solvolysis rate constants and their standard deviations, given in Table I, were ob-

(1) Part I, THIS JOURNAL, **74**, 5285 (1952).

(2) Part II, *ibid.*, **75**, 2925 (1953).

(3) Obtained from the Stuart Oxygen Company on allocation from the United States Atomic Energy Commission.

(4) Preparation suggested by Professor C. E. May.

tained from the slope of the least squares plot of t vs. $\log b/(b - x)$.

In the olefin determinations a series of tubes was filled with a solution of each of the halides in the same 80% aqueous alcohol solution containing just enough sodium hydroxide to ensure that the solution remained basic throughout. These tubes were sealed off and a set of each was allowed to react for 10 to 20 half-lives at each of the four temperatures. The amount of olefin in each tube was determined by the reaction with standard bromine in cold chloroform[2] and the total reaction determined by titration of the remaining base. The olefin fractions were calculated from these values. Whereas the absolute accuracy would be somewhat poorer the parallel nature of the experiments made the reproducibility and the relative accuracy of the olefin fractions of the order of 0.005.

TABLE I

RATE DATA FOR THE SOLVOLYSIS OF 2,3-DIMETHYL-2-CHLOROBUTANE (I) AND ITS 2-DEUTERO ANALOG II IN 80% AQUEOUS ALCOHOL

Temperature, °C.	25.00	36.00	45.00	55.00
Number of points				
I	13	13	14	14
II	15	13	14	15
K (10^{-6} sec.$^{-1}$)				
I	8.680	35.01	98.74	294.2
II	6.765	28.54	82.56	250.4
Std. deviation of K				
I	0.053	0.18	0.28	1.4
II	0.055	0.17	0.17	1.0
Olefin fractions				
I	0.693	0.701	0.708	0.712
II	0.630	0.640	0.660	0.665

Table II gives rate data at four different temperatures for the solvolysis of t-amyl and t-butyl chlorides taken, under the same conditions and in the same solvent as used for the above compounds, for purposes of comparison. The rate constants show reasonably good agreement with values already reported.[5,6,7] Table III gives for all four compounds the Arrhenius equation parameters and their standard deviations, calculated by the least squares method from the plot of $1/T$ vs. log k. Since the rate constants were taken at the same four temperatures for each of the two pairs of compounds the *differences* in activation energy and frequency factors and their standard deviations in the two cases were determined from the slope and intercept of the least squares plot of log k'/k vs. $1/T$. This procedure should give a more accurate measure of the differences in each of the two cases compared. There is a slight disagreement with Hughes, Ingold and co-workers[8] on the absolute magnitude of the Arrhenius parameters in the solvolysis of t-butyl and t-amyl chlorides. These could arise easily from small differences in rate constants due to slightly different techniques or to slightly different temperature calibration between the two investigations. The agreement on the difference between these parameters in the two cases, which is the important experimental result, is well within the expected error of either determination.

TABLE II

RATE DATA FOR THE SOLVOLYSIS OF t-BUTYL AND t-AMYL CHLORIDES IN 80% AQUEOUS ALCOHOL

Temperature, °C.	25.00	35.00	45.00	55.00
No. of points				
t-Butyl	14	13	12	14
t-Amyl	16	14	14	15
K (10^{-6} sec.$^{-1}$)				
t-Butyl	8.919	30.74	97.52	284.2
t-Amyl	15.092	52.32	161.6	453.5
Std. dev. of K				
t-Butyl	0.029	0.04	1.2	0.9
t-Amyl	0.053	0.04	0.3	2.0

TABLE III

ARRHENIUS PARAMETERS FOR SOLVOLYSIS IN 80% AQUEOUS ALCOHOL

Compound	t-Butyl chloride	t-Amyl chloride	I	II
E_a (kcal.)	22.43	22.05	22.80	23.37
Std. dev. of E_a	0.06	0.19	0.11	0.17
Log freq. factor (A) (sec.$^{-1}$)	11.397	11.45	11.659	11.969
Std. dev.,	0.004	0.01	0.007	0.01
$\Delta E_a{}^a$,		0.470		0.584
Std. dev.,		.126		.069
log $A'/A_a{}^a$		.10		.32
Std. dev.,		.06		.03

^{a} These differences, between t-butyl chloride and t-amyl chloride, and between I and II were determined from the least squares plot of log k'/k vs. $1/T$ (see text).

(5) H. C. Brown and R. S. Fletcher, THIS JOURNAL, 71, 1845 (1949).
(6) H. C. Brown and R. S. Fletcher, *ibid.*, 72, 1223 (1950).
(7) E. D. Hughes and B. J. MacNulty, *J. Chem. Soc.*, 1283 (1937).
(8) K. A. Cooper, E. D. Hughes, C. K. Ingold, G. A. Maw and B. J. MacNulty, *ibid.*, 2049 (1948).

The difference in energy of activation between I and II was determined to be about 580 cal. while the difference in the log of the frequency factors is 0.32 ± 0.03 unit. These effects combine to give a difference in free energy of activation at 25° of about 147 cal.

Thus the treatment given before,[2] with the approximate calculations based only on relative rates at 25°, which assumed a constant frequency factor evidently gave values for the change in characteristics of the β-C–H bonds which were much too low. Because of the large experimental error involved in resolving the rate effect into its Arrhenius parameters and because of the insurmountable difficulties involved in detailed theoretical treatment of such a complex system, accurate calculation of changes in bond properties on activation do not seem possible. Nevertheless, the mechanistically significant conclusion (made in the earlier paper) that rather drastic loosening of the β-C–H bonds accompanies the activation process seems well founded.

In Table IV are summarized, in terms of free energy of activation changes, the effects of deuteration on the solvolysis rates at 25° of the tertiary alkyl halides studied.

TABLE IV

CHANGES IN THE FREE ENERGIES OF ACTIVATION DUE TO DEUTERATION

R in R–C(CH$_3$)$_2$Cl	ΔF_a on deuteration of β-position (cal.)	ΔF_a per β-C–H bond (cal.)
CβH$_3$—	168	56
CH$_3$—CβH$_2$—	190	95
(CH$_3$)$_2$=CβH—	156	156

The value for the tertiary C–H bond is seen to fit in as was to be expected on the basis of the results of the earlier paper.[2] The trend in the values per C–H bond is shown to increase regularly as the stability of the corresponding olefin increases, from the CH$_3$– to the CH$_2$ to the CH group. The overall effect, because of the diminishing number of β-C–H bonds in the series, gives a maximum for the –CH$_2$ group with the other two about equal.

The hypothesis of elimination type driving forces and the detailed modifications proposed earlier[2] for the mechanism of the S_N1-E1 processes suggest that the principal difference in rates in this series of tertiary halides with increasing β-branching is due to the changing contribution to the solvolysis driving force from the elimination part of the reaction. It is further suggested that this contribution would vary in proportion to the observed isotope rate effect of β-deuterium substitution. Or, to phrase it another way, the isotope rate effect of β-deuterium substitution should be a relative measure of the amount of electron release from the β-C–H bond to the central carbon atom. If these suggestions actually obtain it should be possible to correlate the solvolysis rates of a series of tertiary carbinyl chlorides containing methyl, ethyl and isopropyl groups with the isotope rate effect observed for deuterium substitution in these groups. The graph shows a plot of the rates of solvolysis of five different tertiary carbinyl chlorides containing

only methyl, ethyl and no more than one isopropyl group[9] against what might be called an "arbitrary" parameter which is the sum of the parameters for the three substituent groups in the carbinyl chloride. These group parameters are the values taken from column 1 of Table IV. The parameter for tertiary butyl chloride is, for example, 3 × 168 or 504; for dimethylisopropylcarbinyl chloride, (2 × 168) + (1 × 156) or 492.

There is uncertainty in rate assignment for diethylisopropylcarbinyl chloride[8] but either constant would be fairly close to the line. The assignment of rate constant to structure is uncertain also in the case of methyldiisopropylcarbinyl chloride[8] and triisopropylcarbinyl chloride.[10] Both of these rate constants are apparently much too large to fall near the line. However, it is interesting to note that if the assignments made by Brown in the former case were reversed, this compound would be at point number 1 in the graph, almost on the line. Under any circumstance, after definite assignments can be made, this correlation should be useful in determining the importance of the B strain effect[5,6] or rearrangement forces[10] in the series containing an increasing number of isopropyl groups.

The fact that t-butyldimethylcarbinyl chloride reacts near the same rate as t-butyl chloride indicates, because of the presumed lowered effectiveness of normal elimination type driving forces, that either steric and/or rearrangement forces are important in this compound. A possible method of correlating this compound into the series is one of the objects of further investigation.

After this work was in progress Lewis and Boozer[11] reported the observation of a similar isotope rate effect of β-deuterium substitution in the decomposition of a secondary alkyl chlorosulfite. The origin of this effect is undoubtedly the same as that in the compounds reported here and indicates that elimination type driving forces are of comparable importance in the solvolysis of secondary alkyl compounds.[12]

There are two principal lines of evidence relating to the subject of hyperconjugation.[13] The first consists of mainly physical evidence (bond lengths, resonance energies, spectra, etc.) relating to the ground state of the molecule. The second consists of chemical evidence from reaction rate studies. It appears that evidence from the first category offers no strong distinction between the hyperconjugative abilities of various alkyl groups, while the idea was initially proposed on the basis of evidence from rate studies that the effectiveness of
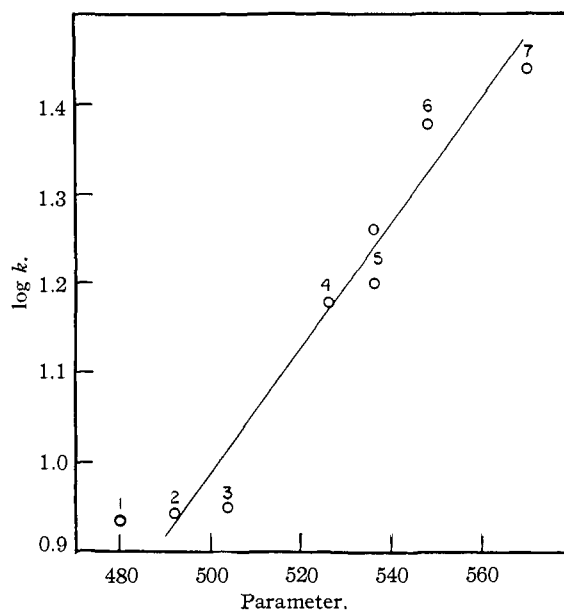
(9) Rate data taken from this work and reference 7.

(10) P. D. Bartlett, *Bull. soc. chim. France*, 5e, **18**, C100 (1951).

(11) E. S. Lewis and C. E. Boozer, This Journal, **74**, 6306 (1952).

(12) Another possible explanation of these phenomena apparently preferred by Lewis and Boozer,[11] attributes the β-C–H bond stretching to hyperconjugation alone and does not explicitly involve solvent attack at these sites. The isotope rate effect for deuterium substitution in a β-methyl, methylene or methinyl group does not vary according to the conventional hyperconjugative sequence, but as explained above does vary in the way expected if partial elimination is occurring. It may be that hyperconjugation theory can be modified slightly to take this into account, but on the basis of present knowledge the author prefers the explanation given above which involves solvation.

(13) J. W. Baker, "Hyperconjugation," Oxford University Press, London, 1952.

Fig. 1.—Plot of log solvolysis k (10^{-6} sec.$^{-1}$) in 80% aqueous alcohol at 25° *vs.* "isotope rate effect parameter." The points represent the following carbinyl chlorides: (1) see text, (2) dimethylisopropyl, (3) trimethyl, (4) dimethylethyl, (5) diethylisopropyl, (6) diethylmethyl, (7) triethyl.

electron release of alkyl groups sometimes varied in the order $CH_3 > CH_2$—CH_2—> $(CH_3)_2$—CH_2—> $(CH_3)_3C$—. It is in just such experiments that the effect herein proposed to explain the relative rates of β-branched tertiary alkyl halides, could be operating (but not, presumably, in experiments relating to the first category). It is relevant that Kloosterziel and Backer[14] have reported that the Hammett sigma constant for a para methyl group, determined from reaction rate studies, depended on the polarity of the medium, being more negative in the more polar medium. Although the subject obviously needs much more investigation before any generalizations can be made, it may be that hyperconjugative effects observed in physical measurements relating to the ground state of the molecule are due to electronegativity differences or to a delocalizing effect such as described by Coulson,[15] but in which there is not much difference between the effectiveness of a β-C–H or a β-C–C link. On the other hand, in studies relating to polar reactions where the magnitude of the effect depends on the number and kind of C–H bonds in hyperconjugation with the reaction center solvation forces, such as described previously,[2] may exert the governing influence or at least act to strengthen the hyperconjugative effect.

Experimental Part

Kinetic Measurements.—A modification of the aliquot method of Hughes and MacNulty[6] was used. One hundred milliliters of 80% aqueous alcohol was placed in a 250-ml. long-neck flask and immersed in the thermostat for one hour or longer. At zero time about 0.6 ml. of the halide

(14) H. Kloosterziel and H. J. Backer, This Journal, **74**, 5806 (1952).

(15) C. A. Coulson, "Valence," Oxford University Press, London, 1952, pp. 310–314.

was quickly pipetted in and the reaction mixture shaken vigorously. At suitable intervals, 5-ml. samples were withdrawn for titration of the developed acid using *ca.* 0.02 *N* standard sodium hydroxide solution with methyl red as the indicator. The total halide present was determined from an "infinity" titration made after a lapse of ten to twenty half-lives. The rate constants were determined from the least squares plot of log $b/(b - x)$ *vs.* t where b is the value of the infinity titration and x the value of the titration of the sample taken at time t. All the bath temperatures were set by Beckmann thermometers standardized in the bath against the same platinum resistance thermometer and Mueller bridge arrangement, sensitive to a few ten-thousandths of a degree. The temperature accuracy, not limited by the calibration standard, should be of the order of ±0.01° or less.

Materials.—The 80% aqueous alcohol was prepared by mixing eight volumes of anhydrous ethanol and two volumes of water. Dimethylisopropylcarbinol, b.p. 117° (750 mm.), n^{25}D 1.4155, was prepared *via* the Grignard reaction from methyl isopropyl ketone and methyl iodide. Dimethylisopropylcarbinyl chloride, b.p. 110° (750 mm.), n^{25}D

1.4178, was made by treatment of the alcohol with concd. hydrochloric acid. The *t*-amyl chloride, b.p. 84.5° (740 mm.), n^{25}D 1.4036, and the *t*-butyl chloride, b.p. 50.5° (740 mm.), n^{25}D 1.3855, were commercial products. Tetramethylethylene, b.p. 71–72° (750 mm.), n^{25}D 1.4095, was prepared by distillation from a mixture of phosphoric acid and dimethylisopropylcarbinol. All of the above organic compounds, except the ethanol and the methyl iodide, were carefully fractionated through a 50 × 1 cm. glass helix packed column with partial take-off head.

Preparation of 3-Deutero-2,3-dimethyl-2-chlorobutane.— A sample of 2.0 g. (0.10 mole) of deuterium oxide was dropped slowly, over a period of 48 hr., into a solution of 22.0 g. (0.28 mole) of acetyl chloride and 7.3 g. (0.087 mole) of tetramethylethylene. After the addition was complete the solution was refluxed for two hours, hydrolyzed on ice and extracted with ether. The ether solution was dried with potassium carbonate and the product recovered by distillation; b.p. 109.5–110° (740 mm.), n^{25}D 1.4182, yield 7.5 g. (0.062 mole), 72%.

BLOOMINGTON, INDIANA

Further Studies on Silicon-containing Carbonyl Compounds: Diketones, Ketoesters and Cyclic Unsaturated Ketones[1]

BY LEO H. SOMMER AND RICHARD P. PIOCH[2]

The use of Me₃SiCH₂CH₂COMe and Me₃SiCH₂CH₂CO₂Et as starting materials in a variety of condensation reactions has permitted the synthesis of a number of new silicon-containing carbonyl compounds which include β-diketones and their copper chelates, β-ketoesters, cyclic α,β-unsaturated ketones, pyrazolones, a δ-diketone and a furoic ester.

It has been demonstrated that organosilicon carbonyl compounds having the structure Si—C—C=O readily undergo cleavage of the organofunctional group from silicon by electrophilic and nucleophilic reagents.[3]
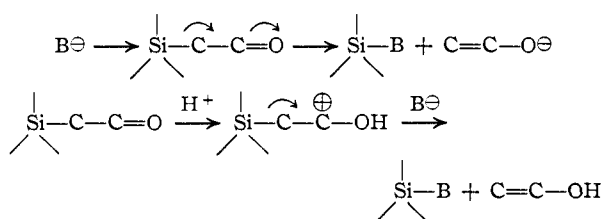
Thus, while trimethylsilylacetone, Me₃SiCH₂COCH₃, recently has been synthesized, attempts to prepare the 2,4-dinitrophenylhydrazone derivative under the usual acidic conditions employed gave instead the derivative of acetone.[4] Further, ethyl trimethylsilylacetate, Me₃SiCH₂CO₂Et, also undergoes cleavage of the carboethoxymethyl group from silicon with acids and bases.[3] Because of the fact that ketones and esters of the type Si—C—C—C=O are structurally incapable of undergoing cleavage of the organo-functional group from silicon by the simple electronic processes shown above, a study of these compounds and their reactions has been undertaken.

Application of the acetoacetic ester synthesis to iodomethyltrimethylsilane in previous work gave good yields of the following monoketones[3]: Me₃SiCH₂CH₂COCH₃, Me₃SiCH₂CH(CH₃)COCH₃ and Me₃SiCH₂CH(C₂H₅)COCH₃. Self-condensation of ethyl β-trimethylsilylpropionate using the excellent reagent of Frostick and Hauser, diisopropylaminomagnesium bromide,[5] gave a symmetrical ketone containing two silicon atoms, Me₃SiCH₂CH₂COCH₂CH₂SiMe₃.[6] Since these syntheses, which were carried out in the presence of strong bases or acids, confirmed our conclusions based on the above mechanistic reasoning, it was of interest to attempt the synthesis of a group of carbonyl compounds of more complex nature, including diketones, ketoesters and cyclic unsaturated ketones.

The methods available for the preparation of such carbonyl compounds generally involve esters and ketones as starting material. In the present work, ethyl β-trimethylsilylpropionate[3] and 5,5-dimethyl-5-silahexane-2-one were used. For the preparation of the latter, a convenient method[7] involving the low-temperature (−65°) reaction of β-trimethylsilylpropionyl chloride with methylmagnesium bromide in the presence of a small amount of ferric chloride gave the desired ketone in good yield.

Synthesis of β-diketones containing silicon was of interest in view of the fact that these compounds are excellent chelating agents for metal ions and

(1) Paper 40 in a series on organosilicon chemistry. For Paper 39 see THIS JOURNAL, **76**, 1186 (1954).

(2) Taken from the Ph.D. thesis of R. P. Pioch, The Pennsylvania State College, 1952.

(3) *Cf.* L. H. Sommer and N. S. Marans, THIS JOURNAL, **72**, 1935 (1950).

(4) C. R. Hauser and C. R. Hance. *ibid.*, **74**, 5091 (1952).

(5) F. C. Frostick and C. R. Hauser, *ibid.*, **71**, 1350 (1949).

(6) L. H. Sommer. R. P. Pioch, N. S. Marans, G. M. Goldberg. J. Rockett and J. Kerlin, *ibid.*, **75**, 2932 (1953).

(7) W. C. Percival, R. B. Wagner and N. C. Cook, *ibid.*, **75**, 3731 (1953).