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The Effects of Deuterium Substitution on the Rates of Organic Reactions. V. Hydrolysis of α-Deutero Ketals[1]

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A study of the effect of deuterium substitution in the α-positions on the rates of hydrolysis of the diethyl ketals of acetone, methyl ethyl ketone, methyl isopropyl ketone and phenoxyacetone has been made. It has been found that the magnitude of the effect is solvent dependent and varies according to the nature of the substituents on the α-carbon atom. This is in general agreement with the results previously obtained for secondary deuterium isotope rate effects on the solvolysis of tertiary alkyl halides, although the rate effects are smaller in the present case. The results are interpreted as indicating that the assumption of Kreevoy and Taft, that the hyperconjugative release of electrons by a C–H bond is independent of the nature of the other substituents on the C-atom, is not quite correct.

The substitution of deuterium for β-situated hydrogen has been shown to have a marked retarding effect on the solvolysis rates of certain tertiary alkyl chlorides and related compounds. This effect has been explained tentatively in terms of hyperconjugation[2] and of hyperconjugation assisted by β-hydrogen solvation.[3]

It has further been shown that the effect is cumulative as the degree of β-deuterium substitution increases and that it is dependent on the nature of the other groups on the carbon which is the site of isotopic substitution.[3] For example, substitution of a deuterium atom for a secondary hydrogen atom in an ethyl group gives a smaller effect than obtains when the tertiary atom of an isopropyl group is replaced. Replacement of a primary hydrogen atom of a methyl group leads to a still smaller effect.

The recent work of Kreevoy and Taft[4] gives some of the best evidence in the literature for the effect of hyperconjugation on reaction rates. These authors were able to correlate the hydrolysis rates of a number of diethyl acetals and ketals with the Taft equation in the form $\log k/k_0 = \rho^*\Sigma\sigma^* + (n - 6)h$, where k refers to the hydrolysis rate of any of the ketals or acetals studied, k_0 refers to the hydrolysis rate of diethyl acetonal, ρ^* is a reaction constant, σ^* is a substituent constant characteristic of the substituent on the ketal linkage, n is the number of α-C–H bonds in the acetal or ketal and h is a constant characteristic of the acceleration of the solvolysis rate due to the hyperconjugative effect of one C–H bond. The important thing to note for purposes of the present discussion is that the equation rather successfully correlates a large number of rate constants differing in magnitude over a wide range, with the assumption that each α-C–H bond hyperconjugates the same amount regardless of the nature of its environment in the molecule. Since this leads to a conclusion different from that obtained from the secondary deuterium isotope rate effects, *if* one assumes that the *variations* noted in the latter are due to variations in hyperconjugation, it was of interest to us to locate the apparent discrepancy more precisely by measuring the isotope effects of deuterium substitution in different groups on the hydrolysis rates of ketals.

The deuterated ketals were made by treating the deuterated ketones with ethyl orthoformate, ethanol-*d* and a trace of strong acid catalyst. The deuterated ketones were made by repeated base-catalyzed exchange with deuterium oxide. The ketones were deuterated in the α-position to the extent of 95–97% before being used in the ketal preparation. During the ketal preparations some spurious exchange apparently lowered the deuterium content and the deuterated ketals were not of the same high degree of isotopic purity. Table I gives the deuterium analyses for the deuterated ketals used.

TABLE I

DEUTERIUM ANALYSES OF KETALS

Ketal of	D, %	Atoms D/mole	Deut. of α-pos., %
Acetone	30.56	4.88	81.3
Methyl ethyl ketone	22.46	4.04	80.8
Methyl isopropyl ketone	13.23	2.65	66.2
Phenoxyacetone	21.19	4.24	84.8

The rates of hydrolysis of the ketals of acetone, methyl ethyl ketone and their deuterated analogs were first measured in an acetic acid–sodium acetate buffer in 50% (by weight) aqueous dioxane, the solvent used by Kreevoy and Taft. In order to make the isotope rate effects as large as possible, subsequent measurements on all of the compounds were done in 90% dioxane–10% water solution. The phenoxyacetone ketal hydrolyses were catalyzed by dilute hydrochloric acid and the others by a dichloroacetic acid–sodium acetate buffer.

The rate measurements were mainly made with a dilatometer, although several constants obtained in this way were checked using a spectrophotometric method. The rate constants were calculated by the statistical method for first-order reactions described by DeTar.[5] Fifty to seventy points were used in calculating the results for each run. The computation was programmed for an IBM 650 Magnetic Drum Data Processing Machine. The program yielded the rate constant, the constants a and b and the standard deviations for each. It is important to note that the statistical method successfully overcomes difficulties in reproducing rate constants which are associated with errors in

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(2) E. S. Lewis and C. E. Boozer, THIS JOURNAL, **76**, 791 (1954).

(3) V. J. Shiner, Jr., *ibid.*, (a) **75**, 2925 (1953); (b) **76**, 1603 (1954).

(4) M. M. Kreevoy and R. W. Taft, Jr., *ibid.*, **77**, 5590 (1955).

(5) D. F. DeTar, *ibid.*, **78**, 3911 (1956).

the zero and infinity readings. As a result the variations in the same rate constants from run to run are of the same order as the standard errors in a given run. The hydrolysis rate for each compound was measured in from two to five different runs and several times with different preparations of the ketals. With a few exceptions all of the reactions in a given solvent type were carried out with solvent from the same master batch. The common impurities encountered in the ketals, the hydrolysis products, ethyl formate and ethyl orthoformate do not affect the observed rates if they are present in only small amounts. Ethyl formate hydrolyzes too slowly and ethyl orthoformate too rapidly. However, the impurities would affect the deuterium analyses, so care was taken to obtain pure compounds. Gas chromatography analyses showed that the deuterated ketals were about 95 mole % pure. More than half of the impurities was accounted for as hydrolysis products which would not strongly affect the deuterium analyses. The constants obtained are summarized in Tables II and III.

TABLE II

HYDROLYSIS RATES OF KETALS IN 90% DIOXANE–10% WATER AT 25°

Diethyl ketal of	k_1, 10^{-4} sec.$^{-1}$	Std. error	No. of runs
Acetone[a]	3.67	0.01	3
Acetone-d_6[a]	3.27	.01	5
Methyl ethyl ketone[a]	2.73	.02	3
Methyl ethyl ketone-d_5[a]	2.37	.01	2
Methyl isopropyl ketone[a]	3.20	.02	3
Methyl isopropyl ketone-d_4[a]	2.89	.01	3
Phenoxyacetone[b]	3.52	.03	3
Phenoxyacetone[b,c]	3.52	.02	2
Phenoxyacetone-d_5[b]	2.80	.01	2

[a] Solution 0.05 *N* in dichloroacetic acid and 0.02 *N* in sodium acetate. [b] Solution 0.00786 *N* in hydrogen chloride. [c] Measured spectrophotometrically.

TABLE III

HYDROLYSIS RATES OF KETALS IN 50% DIOXANE–50% WATER AT 25°

Diethyl ketal of	k_1[a]	[H+]	k_2, l./mole/sec. This work	Ref. 4[b]
Acetone[c]	2.31	3.04×10^{-7}	7.60×10^2	7.52×10^2
Acetone-d_6[c]	2.09	3.04×10^{-7}	6.87×10^2	
Methyl ethyl ketone[c]	2.34	3.04×10^{-7}	7.70×10^2	7.2×10^2
Methyl ethyl ketone-d_6[c]	2.12	3.04×10^{-7}	6.96×10^2	
Phenoxyacetone[d]	4.04	1.28×10^{-3}	0.315	0.350

[a] Units of 10^{-4} sec.$^{-1}$; std. errors are all about 0.01. [b] Data of Kreevoy and Taft, ref. 4. [c] Measured dilatometrically in buffer solutions 0.02 *N* in sodium acetate and 0.01 *N* in acetic acid, [H+] calculated by method of Kreevoy and Taft. [d] Measured spectrophotometrically because of low solubility of ketal; solution 0.001283 *N* in $HClO_4$.

Table III shows that the rate constants obtained in this work for diethylacetonal and diethylbutanonal dilatometrically and for diethylphenoxyacetonal spectrophotometrically agree reasonably well with those obtained spectrophotometrically by Kreevoy and Taft for these compounds. Table II also shows agreement between hydrolysis rate constants obtained in this work for diethylphenoxyacetonal by the spectrophotometric and dilatometric methods. Table IV gives a summary of the isotope rate effects observed for the different compounds in 90% dioxane–10% water at 25°. The observed rate ratios, the changes in free energy of activation due to the amount of deuteration actually obtained (calculated by the formula $\Delta\Delta F\text{a} = RT \ln k_H/k_D$) and the predicted free energy of activation change due to complete deuteration of the α-positions are given. These last figures were obtained from the observed free energy differences and the deuterium analyses given in Table I by a proportional extrapolation.

TABLE IV

SUMMARY OF ISOTOPE RATE EFFECTS DUE TO α-DEUTERATION ON HYDROLYSIS OF KETALS AT 25°

Diethyl ketal of	K_H/K_D (obs.)	$\Delta\Delta F$a (obsd.)	$\Delta\Delta F$a (cor.)[a]
Acetone[b]	1.12	67.2	82.5
Acetone[c]	1.10		
Methyl ethyl ketone[b]	1.15	83.0	102.6
Methyl ethyl ketone[c]	1.10		
Methyl isopropyl ketone[b]	1.11	61.9	93.5
Phenoxyacetone[b]	1.25	132.0	156.0

[a] Corrected to represent complete α-deuteration; units are calories. [b] In 90% dioxane–10% water. [c] In 50% dioxane–50% water.

Table V shows how the data in the last column of Table IV may be broken down to give the isotope rate effects due to deuteration of the α-position of each group and due to each deuterium atom substituted. This separation is based on the assumption that the free energy of activation effects of deuteration are linearly accumulative and that the methyl group shows a constant effect (for a given reaction) from compound to compound. The available data, obtained in the study of secondary deuterium isotope rate effects on the hydrolysis of tertiary alkyl halides,[3] which test these two assumptions, indicate that they are at least approximately correct. The first three entries in Table V show that the isotope rate effect per α-deuterium atom increases in the series of groups methyl (14 cal.), ethyl (30 cal.), isopropyl (51 cal.) in about the same way that it does in these three groups in the hydrolysis of tertiary alkyl halides where the free energy of activation effects per deuterium atom are, in order, 56, 96 and 156 calories. Thus the two cases are strikingly similar. The isotope effects are smaller in the hydrolysis of ketals because the carbon atom to which the groups are attached develops a smaller degree of unsaturation in the ketal hydrolysis transition state, which forms a carbonium–oxonium ion, than it does in the alkyl chloride solvolysis transition state, which forms a carbonium ion.

TABLE V

ISOTOPE RATE EFFECTS IN KETAL HYDROLYSES DUE TO α-DEUTERATION OF DIFFERENT GROUPS

Group deuterated	$\Delta\Delta F$a/group[a]	$\Delta\Delta F$a/D atom[a]
Methyl	42.3	14
Ethyl	61.3	30
Isopropyl	51.2	51
Phenoxymethyl	115.0	57

[a] Units are calories.

The last entry in Table V summarizes the data which extend our present knowledge of the effects of substituents on secondary isotope rate effects to include the interesting example of the phenoxy group. This substituent increases the isotope rate effect of deuteration more than do two methyl groups. Since the methyl group is an inductive electron releaser while the phenoxy group is an inductive electron attractor, it would seem that the similar effects of the two groups on the isotope rate effect would be related to their conjugative electron-releasing powers which operate in the same direction for both but to a greater extent in the phenoxy group. Thus the group effects on the isotope rate effect might be attributed to the extra stabilization of hyperconjugative canonical forms by resonance (conjugation and hyperconjugation). These effects are viewed as being intrinsically similar to second-order hyperconjugation which shows up, for example, in the alternation effect.[6]

The isotope effects were observed to be larger in 90% dioxane–10% water than in 50% dioxane–50% water. This trend is in the same direction as that already observed for solvent effects on secondary isotope rate effects in the solvolysis of organic halides.[2,3,7]

Using the Taft–Hammett equation and the rate constants obtained in this work for acetonal, methyl ethyl ketone ketal and phenoxyacetonal, values for ρ^* and h can be calculated for the reaction in each of the two solvents used. The calculated value for h is appreciably larger in the less polar solvent, so h and the isotope rate effect apparently show the same gross dependence on solvent composition. Unexpectedly, ρ^* turned out to be slightly smaller in the less polar solvent, but the difference was small and apparently within the experimental error. These values are not given because they are not calculated as averages for a representative number of points and their absolute magnitude is not very significant, but they should be accurate enough to show the correct relationship between the parameters for the two solvents.

In conclusion, it seems that the apparent discrepancy noted in the introduction between the interpretation of the substituent effects on secondary deuterium isotope rate effects as being due to variations in hyperconjugation and the use of the Taft h parameter as a measure of hyperconjugation is inherent in the methods themselves and not in the reaction systems studied. It appears that the Kreevoy–Taft assumption of a constant value of h characteristic of every C–H bond may be an approximation and that the value obtained by the statistical method used is an average one which smooths out the variations among the different cases. Perhaps the remaining deviations of the points from the line are due to variations in h values.

It is not considered that the secondary deuterium isotope rate effects are a direct relative measure of hyperconjugation.[8] At least two other factors, not yet fully investigated, are recognized as influencing the magnitude of these secondary isotope rate effects. The first of these is the solvent effect[3,7] and the second is the isotope effect on the frequency factor of the Arrhenius equation. Carbon–hydrogen bond stretching, presumably resulting from increased hyperconjugation in the transition state, shows up most directly in the activation energy term of the isotope rate effect. The observed rate effect is of course a combination of the activation and frequency factor effects. In the cases where the Arrhenius parameters of the secondary isotope rate effects have been measured, it has turned out that the activation energy effect was present and affected the rate ratios, in the temperature range in which they were observed, in the direction observed. However, this effect was, in each case, partly cancelled by a frequency factor effect in the opposite direction. This suggests that at some temperature the frequency factor and activation energy effects would cancel and no isotope rate effect would be observed. At a higher temperature a negative rate effect would be found. This "cross-over" temperature might be different in different reaction systems. The most fundamental (but more difficulty obtained) experimental quantity is the isotope activation energy effect. In each of the cases that have been measured thus far this has paralleled the isotope rate effect at the temperatures used. This relationship, which will not always hold, is a necessary condition for the isotope rate effects to be relative measures of hyperconjugation. However, in comparing closely related reactions in the same solvent at the same temperature it seems that the isotope rate effect variations are most reasonably attributed to variations in hyperconjugation.

Experimental

Purification of Commercial Chemicals.—The following compounds were purified by distillation through an 88 × 1.9 cm. column packed with $^1/_2''$ glass helices: ethyl orthoformate, b.p. 143–144° (740 mm.); methyl ethyl ketone, b.p. 78.5° (740 mm.); and methyl isopropyl ketone, b.p. 92.3° (740 mm.). Dioxane was purified according to the method of Fieser[9] and fractionated through the 88 × 1.9 cm. column. Absolute alcohol was obtained by distilling added benzene from commercial absolute ethanol through a packed column. The ternary azeotrope (b.p. 64.9°), the ethanol–benzene azeotrope (b.p. 68.2°) and a foreshot of ethyl alcohol (b.p. 78.5°) were removed before the material to be used was collected.

Deuterium Oxide.—The deuterium oxide was obtained from the Stuart Oxygen Co. and was specified to be 99.5% isotopically pure.

Phenoxyacetone.—This compound was prepared according to the method of Hurd and Perletz[10] and vacuum distilled. It was then fractionally distilled through a spinning band column and the product collected at 125° (18 mm.), over-all yield 48%. The semicarbazone derivative gave m.p. 175–176°, reported[11] 173°.

Deuteration of Ketones.—Deuteroacetone was made by repeated potassium carbonate catalyzed exchange with deuterium oxide. The deuteroacetone was separated from each exchange by distillation. Methyl ethyl ketone was exchanged by refluxing the ketone with deuterium oxide and a little potassium carbonate for 24 hr. The deuterated methyl ethyl ketone–water azeotrope was separated from the deuterium oxide each time by distillation. Methyl isopropyl ketone was exchanged by refluxing with deuterium

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(6) M. J. S. Dewar, "Electronic Theory of Organic Chemistry," Oxford University Press, Oxford, 1949, pp. 157–159.

(7) V. J. Shiner, Jr., and C. J. Verbanic, THIS JOURNAL, **79**, 373 (1957).

(8) C. G. Swain, T. E. C. Knee and A. J. Kresge, *ibid.*, **79**, 505 (1957).

(9) L. F. Fieser, "Experiments in Organic Chemistry," 2nd Ed., D. C. Heath and Co., New York, N. Y., 1941, pp. 369.

(10) C. D. Hurd and P. Perletz, THIS JOURNAL, **68**, 39 (1946).

(11) R. Stoermer, *Ann.*, **312**, 273 (1900).

oxide and a little potassium carbonate for three days. Deuterated methyl isopropyl ketone was separated from the deuterium oxide by separation of the layers after cooling. Phenoxyacetone was exchanged by refluxing for 24 hr. with a deuterium oxide–dioxane solution to which had been added several drops of triethylamine. Enough dioxane was used so that all of the deuterium oxide could be distilled from the mixture as the dioxane azeotrope and separation was thus accomplished. The exchanges were carried out each time with 5.0 g. (0.25 mole) of deuterium oxide and enough ketone so as to have an equivalent number of exchangeable (alpha) hydrogen atoms. Several successive ketone samples were run through the same sequence of deuterium oxide samples to increase the efficiency of deuterium transfer. The exchanges were continued until the completely α-deuterated ketones were 95–97% isotopically pure as shown by combustion analysis.

Preparation of Ketals.—The method of Carswell and Adkins[12] was used for the preparation of the ketals. These materials had to be distilled carefully at reduced pressures to prevent decomposition to the enol ethers which was apparently promoted by higher temperatures. The Carswell and Adkins procedure which involves the treatment of the ketone with ethyl orthoformate, ethyl alcohol and a little hydrochloric acid had to be modified for the preparation of the deuterated ketals, to include ethanol-*d* instead of ethanol to prevent loss of the deuterium from the deuterated ketones by exchange. This was accomplished as described in the following procedure for the preparation of deuterated phenoxyacetone ketal. The other deuterated ketals were prepared in a similar way. A 39 × 1.0 cm. fractionating column packed with $^1/_{16}''$ glass helices was cleaned and dried by refluxing ethyl orthoformate through it and removing the low-boiling material. In a 100-ml. round-bottomed flask were placed 57 ml. (0.35 mole) of ethyl orthoformate, 3.9 ml. (0.21 mole) of deuterium oxide and one drop of concentrated hydrochloric acid. The flask was attached to the cleaned column, and 17.2 g. of material was distilled out until the temperature reached 76°; theoretical yield of ethyl formate, 15.8 g. The flask was allowed to cool and 15.75 g. (0.10 mole) of deuterated phenoxyacetone and one drop of concentrated hydrochloric acid were added. The mixture was shaken and allowed to stand at room temperature for 11 days and then distilled through a dry spinning band column. Ethyl formate was distilled over at atmospheric pressure and the ethanol-*d* was distilled at 100 mm. Deuterated phenoxyacetone ketal, 19.5 g. (0.087 mole), was collected at 69–71° (0.1 mm.), yield 87%. Combustion deuterium analysis showed the material to contain an average of 4.24 deuterium atoms per molecule.

The yields of the other deuterated ketals varied from 45 to 65%. The boiling points of methyl isopropyl ketone ketal and ethyl orthoformate are very close together so the product obtained in the preparation of the former compound was subjected to partial hydrolysis with deuterium oxide catalyzed by a drop of glacial acetic acid. Enough deuterium oxide was added to hydrolyze about 33% of the material. This hydrolysis should have preferentially removed any ethyl orthoformate impurity. The hydrolysis reaction mixture was redistilled in the spinning band column. Gas chromatography analysis showed the distillate to be 95 mole % or more pure.

Dioxane–Water Solution.—Solutions 90% dioxane–10% water and 50% dioxane–50% water (by weight) were prepared from the dioxane purified as mentioned above and deionized distilled water. The following solutions were made from the 50% dioxane, placed in brown glass-stoppered bottles and stored in an ice-box for use as needed: (1) 0.02 *N* sodium acetate and 0.01 *N* acetic acid, (2) 0.001283 *N* perchloric acid. The following solutions were made from the 90% dioxane solution and similarly stored: (1) 0.02 *N* sodium acetate and 0.05 *N* dichloroacetic acid, (2) 0.00786 *N* hydrogen chloride.

Deuterium analyses were done using the method previously described.[13]

Kinetic Equipment.—The dilatometer consisted of a 125-ml. spherical mixing chamber connected by a long-handled stopcock to a 100-ml. reaction chamber in the shape of a U-tube approximately 34 cm. long and 15 mm. in diameter. The other end of the U-tube was connected to a precision bore capillary tube 30 cm. long and approximately 0.6 mm. inside diameter. The runs were done in a constant temperature water-bath kept in a room at 22° and heated intermittently by an infrared lamp. The temperature was set at 25.00 ± 0.001° with a Beckman thermometer calibrated against a platinum resistance thermometer. The temperature variations were of the order of ±0.002°.

Kinetic Procedure.—The dilatometer was placed in the 25.00° bath, and 105 ml. of solvent was placed in the mixing chamber. After the solvent had come to the temperature of the bath, approximately 1 ml. of the ketal was pipetted into the solution which was then stirred and degassed. Degassing was accomplished by reducing the pressure in the mixing chamber until the solution boiled. Then the reaction mixture was run into the reaction chamber and allowed about 15 minutes to come to temperature. The meniscus was then allowed, by slow opening of the stopcock, to rise into the bottom part of the capillary tube, and readings by a cathetometer of the meniscus heights with time were begun. The reaction half-lives were of the order of 45 min., and readings were taken through the second half-life or longer. The total capillary rise was usually in the range of 5 to 10 cm.

The rate of hydrolysis of phenoxyacetone ketal was measured in several experiments using a spectrophotometric method based on the change in absorption at 295 mμ which accompanies the reaction. The run was done in a flask in the 25.00° bath, and 3-ml. samples were withdrawn periodically and their optical densities measured at 295 mμ in a Beckman DU spectrophotometer.

Calculation of Rate Constants.—The rate constants were calculated by the statistical method described by DeTar.[4] The basic equation which applies is

$$h_i = a + be^{-kt_i}$$

where k is the first-order hydrolysis rate constant, h_i is the cathetometer reading at time t_i, a is equal to the cathetometer reading at infinity and b is equal to the cathetometer reading at zero time minus the infinity reading. The data are fitted to the equation treating a, b and k as disposable parameters chosen so that $\Sigma(h_i \text{ (observed)} - h_i \text{ (calculated)})^2$ is a minimum. This treatment avoids difficulties in reproducing first-order constants which have traditionally been associated with errors in zero and infinity readings. The solution was programmed for an IBM 650 Magnetic Drum Data Processing Machine. The programming was done in the Bell Laboratories interpretive system. The data, consisting of a series of height and a series of corresponding time readings along with an estimate of the infinity height reading, is fed into the machine on punched cards. The machine calculates a trial rate constant and then calculates corrections for the trial constant and for a and b. It then tests these for size, and if the corrections are 0.1% or more, it recycles to calculate another correction. When the correction is small enough, it then calculates the standard errors, punches a, b and k and their standard errors on output cards and takes in the data for the next run. The program for a seventy point run usually takes five to ten minutes machine time depending on the number of successive corrections (usually two to four) it must calculate. This compares with DeTar's estimate of 4 hr. used by an experienced operator to calculate a single set of corrections and the standard errors for a ten point run using a desk calculator. These calculations would not be practical for runs involving many points without an electronic computing machine.

Gas Chromatography Analyses.—The deuterated ketals used were analyzed for impurities using a Fisher–Gulf Partitioner equipped with an 8 ft. column packed with Carbowax supported on powdered firebrick. The column was thermostated at 100°. Elution times for the ketones and ketals (except phenoxyacetone ketal which was not run) were less than 15 minutes. Ethyl orthoformate seemed to decompose a little on the column but gave a characteristic elution pattern. The deuterated ketals were all 95 or more mole % pure with most of the impurities being accounted for as the ketal hydrolysis products.

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[12] H. E. Carswell and H. Adkins, THIS JOURNAL, **50**, 236 (1928).

[13] V. J. Shiner, Jr., *ibid.*, **74**, 5285 (1952).