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Salt Effects in the Reaction between Bromate and Iodide Ions

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The rate of the reaction of bromate with iodide ions has been measured in the presence of different salts. The reaction is accurately first order with respect to BrO_3^- and I^- and second order with respect to H^+. The results for the nitrates of potassium, magnesium and lanthanum can be expressed by

$$\log k = \log k_0 - 2.036 \frac{\sqrt{\mu}}{1 + \sqrt{\mu}} + 1.1\,\mu$$

with individual deviations of the order of 2 to 4%. The sodium and barium nitrates and the potassium perchlorate give similar results. The chlorides give higher rate constants, and this can be interpreted as due to a reaction between bromate and chloride ions. The sulfates give much lower rate constants, due to the formation of the HSO_4^- ion. When the reduction in the hydrogen ion concentration is taken into account, the results for the sulfates are very similar to those for the nitrates at equal cation concentration. Uranyl nitrate has a specific accelerating effect, which is not due to the increase in H^+ concentration produced by the hydrolysis. The rate of the reaction catalyzed by uranyl nitrate seems to be of lower order with respect to the H^+ ion.

In previous papers, the salt effects on the alkaline hydration of condensed phosphates[1,2] and on the reaction between persulfate and iodide[3] have been shown to be very specific and to involve some non-electrostatic factor.[2,4] In these cases the activated complexes have a large negative charge, and this can explain to a certain extent the predominance of the specific effects. We thought it would be of interest to study a reaction in which the activated complex has no charge, and we have chosen the reaction between bromate and iodide. This reaction is known to be first order with respect to both BrO_3^- and I^-, and second order with respect to H^+.[5] It can be assumed that the reaction proceeds through some intermediate steps, such as[5c]

$BrO_3^- + 2H^+ = BrO_2^+ + H_2O$ rapid equilibrium

$BrO_2^+ + I^- = BrO^+ + IO^-$ rate determining
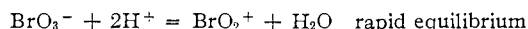
followed by rapid reactions of the ions BrO^+ and IO^- with H^+ and I^-. Independent of any mechanism which can account for the observed orders,

it can be proved that the reaction rate is proportional to the fourth power of the activity coefficient of a monovalent ion. The predicted salt effect therefore has the same magnitude as that predicted for the persulfate–iodide reaction, but it is opposite in sign. Only univalent ions, however, are involved. Deviations from the Debye–Hückel limiting law should therefore start at concentrations greater than for systems involving multivalent ions.[6]

Using an approach similiar to that employed in the case of the other reactions indicated above,[1,3,4,7,8] we have measured the initial rate, to prevent any change in the ionic environment during the reaction. This has been achieved by performing the rate measurements within the first few per cent. of the reaction.

Experimental

Baker and Adamson quality, C.P., acids and Mallinckrodt reagent quality grade salts were used, except for the $Na_3P_3O_9$. This salt was prepared and purified as described in a previous paper.[9] The solutions of $Mg(NO_3)_2$, $MgSO_4$, $La(NO_3)_3$, $MgCl_2$ and $LaCl_3$ were standardized against a solution of ethylenediaminotetraacetic acid using

(1) A. Indelli, Ann. Chim. (Rome), 48, 332 (1958).

(2) A. Indelli, ibid., 46, 717 (1956).

(3) A. Indelli and J. E. Prue, J. Chem. Soc., 107 (1959).

(4) A. Indelli and E. S. Amis, THIS JOURNAL, 82, 332 (1960).

(5) (a) A. A. Noyes, Z. physik. Chem., 19, 599 (1896); (b) G. Magnanini, Gazz. chim. ital., 20, 390 (1890); (c) E. Abel, Helv. Chim. Acta, 33, 785 (1950).

(6) E. A. Guggenheim, Discussions Faraday Soc., 24, 53 (1957).

(7) A. Indelli, Ann. Chim. (Rome), 46, 367 (1956).

(8) A. Indelli, ibid., 47, 586 (1957).

(9) A. Indelli, ibid., 43, 845 (1953).

eriochrome black T as an indicator. The solutions of MgCl₂ and LaCl₃ were also standardized against a solution of AgNO₃, using fluorescein as an indicator. The Na₂S₂O₃ solution was standardized against the stock solution of KBrO₃, which was used, after proper dilution, in the kinetic runs. The HCl and HNO₃ solution were standardized against a sodium hydroxide solution, which had been, in turn, standardized against potassium acid phthalate. All the other solutions were prepared by weighing the solid salts. The experimental technique was the same as used in the study of the persulfate iodide reaction.[3,4] It consisted of adding periodically small, accurately measured, amounts of Na₂S₂O₃ in slight excess with respect to the iodine already present and of timing the reappearance of the iodine by the depolarization of a platinum electrode. The excess of Na₂S₂O₃ added each time had to be very small and approximately constant, and therefore the same precautions as indicated in a previous paper were used.[4] In fact the presence of a larger excess, due to a premature addition of the Na₂S₂O₃ solution, resulted in an increase in the reaction time. This possibly could be due to the reaction

$$S_2O_3^- \longrightarrow S + SO_3^-$$
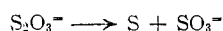
catalyzed by the hydrogen ions and followed by

$$SO_3^- + I_2 + H_2O \longrightarrow SO_4^- + 2H^+ + 2I^-$$
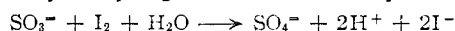
The reaction rate was calculated by plotting the amount of Na₂S₂O₃ added *versus* time. Due to the very small change in the concentrations, straight lines were obtained with good approximation. The fourth order rate constants, obtained by dividing the slopes of the straight lines by the average concentrations during the runs, are reported in Tables I, II and III.

TABLE I

FOURTH ORDER RATE CONSTANTS, $10^{-2}k$ (L.³ EQUIV.⁻³ SEC.⁻¹) FOR THE REACTION OF BrO⁻³ WITH I⁻ AND H⁺ AT 25°

[KBrO₃] = 2.08 × 10⁻⁴, [KI] = 2.50 × 10⁻³, [HCl] = 5.00 × 10⁻³, μ = 0.0077 mole l.⁻¹, 10⁻²k = 7.01 l.³ equiv.⁻² sec.⁻¹

Added salt	0.005 k	μ	0.01 k	μ	0.02 k	μ	0.04 k	μ
NaCl	6.7	0.0127	6.3	0.0177	5.9	0.0277	5.5	0.0477
NaNO₃	6.6	.0127	6.2	.0177	5.5	.0277	4.8	.0477
Na₂SO₄	5.2	.0152	4.1	.0227	2.9	.0377	1.8	.0677
KCl	6.6	.0127	6.2	.0177	5.9	.0277	5.4	.0477
KClO₄	6.6	.0127	6.0	.0177	5.5	.0277	4.9	.0477
KNO₃	6.5	.0127	6.1	.0177	5.6	.0277	4.9	.0477
K₂SO₄	5.2	.0152	4.1	.0227	2.9	.0377	1.8	.0677
MgCl₂	6.5	.0152	6.1	.0227	5.5	.0377	4.9	.0677
LaCl₃	6.2	.0177	5.7	.0277	5.1	.0477	..	....

TABLE II

FOURTH ORDER RATE CONSTANTS, $10^{-2}k$ (L.³ EQUIV.⁻³ SEC.⁻¹) FOR THE REACTION OF BrO₃⁻ WITH I⁻ AND H⁺ AT 25°

[KBrO₃] = 8.33 × 10⁻⁴, [KI] = 2.50 × 10⁻³, [HNO₃] = 2.50 × 10⁻³, μ = 0.0058 mole l.⁻¹, 10⁻²k = 7.31 l.³ equiv.⁻³ sec.⁻¹

Added salt	0.005 k	μ	0.01 k	μ	0.02 k	μ	0.04 k	μ
NaNO₃	6.5	0.0108	6.1	0.0158	5.6	0.0258	5.0	0.0458
Na₂SO₄	5.2	.0133	4.0	.0208	2.8	.0358	1.7	.0658
Na₃P₃O₉	5.8	.0158	5.2	.0258	4.4	.0458	3.5	.0858
KClO₄	6.6	.0108	6.2	.0158	5.5	.0258	4.7	.0458
KNO₃	6.6	.0108	6.2	.0158	5.6	.0258	4.9	.0458
K₂SO₄	5.1	.0133	3.9	.0208	2.7	.0358	1.6	.0658
Mg(NO₃)₂	6.4	.0133	5.9	.0208	5.3	.0358	4.5	.0658
MgSO₄	5.2	.0158	4.1	.0258	3.1	.0458	2.1	.0858
Ba(NO₃)₂	6.6	.0133	5.9	.0208	5.2	.0358	4.4	.0658
La(NO₃)₂	6.3	.0158	5.6	.0258	4.9	.0458	4.3	.0858
UO₂(NO₃)₂	20	.0133	29	.0208	44	.0358	70	.0658

Discussion

The values of k in the absence of added salts are rather close to each other, and the differences are due, to a large extent, to the difference in the

TABLE III

FOURTH ORDER RATE CONSTANTS, $10^{-2}k$ (L.³ EQUIV.⁻³ SEC.⁻¹) FOR THE REACTION OF BrO₃⁻ WITH I⁻ AND H⁺ AT 25°

[KBrO₃], mole/l. × 10⁻⁴	[KI], mole/l. × 10⁻⁴	Acid, mole/l. × 10⁻³	Added salt	Equiv., l.⁻¹	μ	10⁻² k
2.08	5.00	HNO₃	....	..	0.0107	6.5
2.08	5.00	HNO₃	UO₂(NO₃)₂	0.005	.0182	9.0
2.08	5.00	HNO₃	UO₂(NO₃)₂	.01	.0257	11.0
2.08	5.00	HNO₃	UO₂(NO₃)₂	.02	0407	15.0
2.08	5.00	HNO₃	UO₂(NO₃)₂	.04	.0707	19.0
8.33	6.25	HCl	....	..	.0065	6.9
8.33	6.25	HCl	KCl	.02	.0265	6.4
8.33	6.25	HCl	KCl	.04	.0465	6.2
8.33	6.25	HCl	KNO₃	.02	.0265	6.0
8.33	6.25	HCl	KNO₃	.04	.0465	5.3
2.08	0.250	HNO₃	....	..	.0077	7.0
2.08	.250	HNO₃	KNO₃	.02	.0277	5.4
2.08	.250	HNO₃	KNO₃	.04	.0477	4.8
2.08	.250	HNO₃	NaNO₃	.04	.0477	4.9

ionic strength μ. In many cases the effect of μ in a reaction between two ions can be expressed by

$$\log k = \log k_0 + 2A z_a z_b \frac{\sqrt{\mu}}{1 + \sqrt{\mu}} + B\mu \qquad (1)$$

For the reaction between bromate and iodide the factor $2A z_a z_b$ should be replaced by the value 2.036. We can correct, as a first approximation, for the ionic strength effect by calculating the values of k_0', by means of the equation[10]

$$\log k_0' = \log k_0 + 2.036 \frac{\sqrt{\mu}}{1 + \sqrt{\mu}} \qquad (2)$$

Log k'_0 should be a linear function of μ,[10] and for a small change in μ it should be approximately constant. The values of k'_0 in the absence of added salts, calculated from Table I and II, and from the rows 1, 6 and 11 in Table III, are, respectively, 10.23, 10.15, 10.14, 9.82, 10.17, the maximum difference being about 4%. This indicates that the first order rate with respect to BrO₃⁻ and I⁻ and the second order rate with respect to H⁺ hold at least for a fourfold change in concentration of each of the reactants. Mechanisms capable of accounting for these orders in this and in similar reactions have been given by Abel[5c] and by Morgan and coworkers.[11]

The salt effects for corresponding sodium and potassium salts are very similar, and the difference in the rate constants, under otherwise equal conditions, seldom exceeds 2%. The same thing can be said for magnesium and barium nitrates and for potassium perchlorate and nitrate. A plot of log k_0' *versus* μ is given in Fig. 1, for the data for KNO₃, Mg(NO₃)₂ and La(NO₃)₃ taken from Table II. It can be seen that all the points are roughly grouped around a straight line, only one point deviating more than 2%. The data for Mg-(NO₃)₂ and perhaps also for La(NO₃)₃ would fit

(10) (a) F. Bell, R. Gill, D. Holden and W. F. K. Wynne-Jones, *J. Phys. Colloid. Chem.*, **55**, 874 (1951); (b) E. A. Guggenheim and J. E. Prue, "Physicochemical Calculations," North-Holland Publishing Co., Amsterdam. 1956, p. 466.

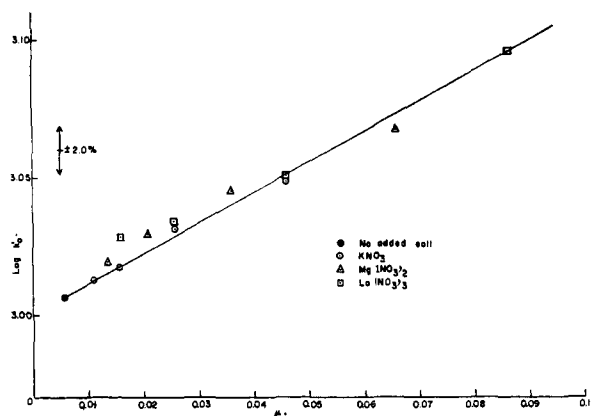(11) K. J. Morgan, M. G. Peard and C. F. Cullis, *J. Chem. Soc.*, 1865 (1951).

Fig. 1.—Log k_0' versus μ for added potassium, magnesium and lanthanum nitrates.

Fig. 2.—Log k_0' versus μ for added potassium, magnesium and lanthanum chlorides.

smooth curves better than the indicated straight line; however, it is difficult to ascertain whether or not some deviations are due to the experimental uncertainty. In fact, we estimate the accuracy of the measurements to be about 2 to 4%. The point (not shown in Fig. 1) for $Ba(NO_3)_2$ at the higher concentration (0.02 M or 0.04 equiv./l.) however, seems to fall significantly below the straight line; a measurement at still higher concentration (0.04 M or 0.08 equiv./l.) gave a value of $10^{-2}k = 3.70$, which also corresponds to a point well below the straight line. Neglecting the differences, relatively small, between cations of the same valence, it seems important to notice that even for different valence of the cations, no great differences are observed in the specific effects, and that the slope of the straight line of Fig. 1 is about 1.1, which seems a rather high value, the usual ones ranging from 0.1 to 0.5.[10b],[12] The first observation is in sharp contrast with what has been observed for some reactions between anions, such as the hydration of trimetaphosphate,[2] the reaction of persulfate with iodide,[3] the alkaline hydrolysis of potassium ethyl oxalate and malonate,[12a] the reaction of bromoacetate with thiosulfate,[13] the isotopic exchange between thiosulfate and tetrathionate[14] and the catalytic rearrangement of tetrathionate,[15] where cations of higher valence have a much larger effect than univalent ones. It appears likely the fact that the activated complex has no charge is responsible for the lack of difference in the action of cations of different valence.

On the other hand, the rate constants for the chlorides are always greater than for the corresponding nitrates. This could be due to a greater value of the B coefficient in equation 1 and, therefore, to a greater specific salt effect. A plot of log k_0' versus μ, for the data for KCl, $MgCl_2$ and $LaCl_3$, taken from Table I, is given in Fig. 2. It can be observed that the points are very much scattered around a single straight line
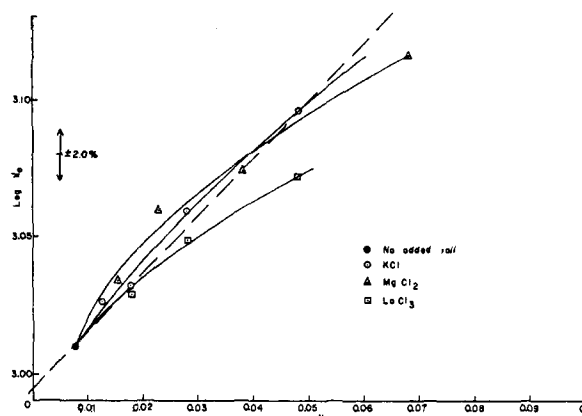
(12) (a) J. L. Hoppé and J. E. Prue, J. Chem. Soc., 1775 (1957); (b) G. Aksnes and J. E. Prue, ibid., 103 (1959).

(13) (a) V. K. LaMer and R. W. Fessenden, This Journal, 54, 2351 (1932); (b) H. G. Davis and V. K. LaMer, J. Chem. Phys., 10, 585 (1942).

(14) A. Fava and G. Pajaro, J. Chim. Phys., 51, 594 (1954).

(15) A. Fava and S. Bresadola, This Journal, 77, 5792 (1955).

(dashed in Fig. 2), but really seem to fit satisfactorily three different curves for the three salts. An alternative explanation is that the ion Cl^- reacts with the ion BrO_3^-, in the same way as the ion I^-, but at a lower rate. In favor of this explanation are these various facts: (1) the slope of the dashed line of Fig. 2 seems to be much larger than usual (2.1); (2) the curve for $LaCl_3$ is much below that for KCl, in correspondence with a smaller concentration of Cl^- at equal ionic strength; the same should be true, to a lesser extent, for $MgCl_2$, but apparently is true only at high concentrations; (3) Skrabal and Weberitsch reported that chloride ion accelerates the rate of the analogous reaction of bromate with bromide[16]; in this case the effect should be much more evident because the reaction rate is much smaller than in the case of the reaction between bromate and iodide. To try to confirm this explanation, the runs 6, 7 and 8 of Table III were performed, in which the lower concentration in iodide and the higher concentration in bromate should favor the reaction between bromate and chloride. The rate constants obtained in the presence of KCl are indeed remarkably higher than in the corresponding condition in Table I. However, a comparison of the rows (9 and 10) of Table III with the values of KNO_3 in Table I shows that an increase in rate at lower iodide concentrations is found even in the presence of nitrates. We were not able to give any explanation of this phenomenon, but a change in the salt effect, corresponding to a change in the concentration of the reactants, already had been observed in the reaction of persulfate with iodide.[3]

In the presence of the sulfate ion the rate constants are much smaller (see Table I and II). A retarding effect of various sulfates has been observed by Weber and Valić[17] in the analogous reaction between ClO_3^- and I^- and by Bray and Liebhafsky in the reaction between BrO_3^- and Br^-.[18]

This retardation must be attributed to the fact that some of the hydrogen ion is sequestered as HSO_4^-. If we assume that this last ion does not

(16) A. Skrabal and S. R. Weberitsch, Monatsh., 36, 211 (1915).

(17) K. Weber and R. Valić, Ber., 72B, 1488 (1939); K. Weber and M. Pichler, ibid., 73B, 415 (1940).

(18) W. C. Bray and H. A. Liebhafsky, This Journal, 57, 51 (1935).

take part in the reaction, we are able to calculate the correct rate constants on the basis of the dissociation constant of the HSO_4^- ion. For the dissociation constant of the HSO_4^- ion, at infinite dilution, we have taken the value of 1.03×10^{-2}, given by Davies and co-workers,[19] and we have calculated the activity coefficients by means of a Güntelberg formula[20]

$$\log f = -Az^2 \frac{\sqrt{\mu}}{1 + \sqrt{\mu}} \qquad (3)$$

We have neglected the association of $SO_4^=$ with Na^+ or K^+. This procedure has been used by Guggenheim, Hope and Prue to calculate the rate of inversion of sucrose in the presence of $NaHSO_4$[21] and has given correct results. For the case of $MgSO_4$, we have also taken in account the association between Mg^{++} and $SO_4^=$ ions, taking for the dissociation constant of the $MgSO_4$ ion pair the value 6.2×10^{-3} given by Dunsmore and James[22] at infinite dilution and calculating the activity coefficients by means of equation 2. A similar calculation also has been performed for $Na_3P_3O_9$, neglecting the formation of the ion pair $NaP_3O_9^=$ and taking the value 9.0×10^{-3}, given by Davies and Monk[23] for the dissociation constant of $HP_3O_9^=$. The method of calculation was the same as that used by Guggenheim, Hope and Prue.[21] The results are reported in Table IV. From a comparison with Tables I and II it can be seen that for the sulfates the corrected rate constants are not in general smaller than the ones for the corresponding nitrates at equal cation concentration, as might have been expected from the greater ionic strength. Instead at the lowest concentration they are almost equal, and at higher concentrations they are somewhat larger. For the sodium trimetaphosphate the rate constants are always larger than those for the sodium nitrate, but the results are not completely reliable because of the uncertainty in the dissociation constant of $HP_3O_9^=$.

It seems therefore that even in the case of the bromate–iodide reaction the salt effects do not depend strictly on the ionic strength. Rather they are, to a certain extent, related to the concentration of cation, and an increase in ionic strength, at equal cation concentration, has, if any, an effect opposite to that predicted by the Brønsted–Christiansen–Scatchard equation.[24] This result was rather unexpected, because even if the salt effects are due mainly to some sort of specific interaction of the added ions with the reactant

(19) C. W. Davies, H. W. Jones and C. B. Monk, Trans. Faraday Soc., 48, 921 (1952).

(20) (a) E. Güntelberg, Z. physik. Chem., 123, 199 (1926); (b) E. A. Guggenheim and T. D. Schindler, J. Phys. Chem., 38, 533 (1934).

(21) E. A. Guggenheim, D. A. L. Hope and J. E. Prue, Trans. Faraday Soc., 51, 1386 (1955).

(22) H. S. Dunsmore and J. C. James, J. Chem. Soc., 1925 (1951).

(23) C. W. Davies and C. B. Monk, ibid., 413 (1949).

(24) E. S. Amis, "Kinetics of Chemical Change in Solution," The Macmillan Co., New York, N. Y., 1949, p. 71 ff.

TABLE IV

FOURTH ORDER RATE CONSTANTS, $10^{-2}k$ (L.[3] EQUIV.$^{-3}$ SEC.$^{-1}$), FOR THE REACTION OF BrO_3^- WITH I^- AND H^+, IN THE PRESENCE OF SULFATES, CORRECTED FOR THE FORMATION OF HSO_4^-, AT $25°$

Added salt	Equiv., 1.$^{-1}$			
	0.005	0.01	0.02	0.04
Na_2SO_4[a]	6.4	6.1	5.6	5.0
K_2SO_4[a]	6.5	6.1	5.8	5.0
Na_2SO_4[b]	6.6	6.2	5.8	5.0
K_2SO_4[b]	6.5	6.1	5.5	4.8
$MgSO_4$[b]	6.4	5.9	5.5	5.0
$Na_3P_3O_9$[b]	6.8	6.6	6.4	5.8

[a] Data from Table I. [b] Data from Table II.

ones, as Olson and Simonson have implicitly postulated,[25] when the reactant ions have opposite sign, we should expect that all the ions would be influential. However, in this case, the specific interactions of the sulfate and the trimetaphosphate ions with the reactant cations, that is with the hydrogen ions, already have been accounted for when calculating the concentrations of the ions HSO_4^- and $HP_3O_9^-$.

The uranyl nitrate shows a large accelerating effect (see Table II) which could be due partly to the hydrolysis and therefore to the increased concentration in H^+. However, Faucherre gives a value for the hydrolysis constant of $UO_2(NO_3)_2$[26] which is by far too small to account for the increase in rate shown in Table II. According to Faucherre the uranyl nitrate hydrolyzes as

$$2UO_2^{++} + 2H_2O \longrightarrow (UO_2OH)_2^{++} + 2H^+$$
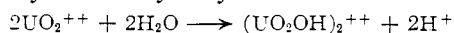
and the equilibrium constant has a value of 1.90×10^{-6} mole 1.$^{-1}$ at an ionic strength of 0.06. From this value, a H^+ concentration of 0.0027 is calculated for a solution containing HNO_3 0.0025 M and $UO_2(NO_3)_2$ 0.02 M, and a value of about 8.5 is calculated for the corresponding rate constant neglecting the salt effect, as compared with the experimental value of 70 given in Table II. As a further check the runs reported in Table III, rows 1, 2, 3, 4 and 5, were made. In these runs the concentration in acid is four times as great as in the runs reported in Table II, and this fact should decrease very strongly the accelerating effect due to the hydrolysis for two reasons: (1) the hydrolysis should be repressed by mass action; (2) the formation of the same amount of acid results in a much smaller percentage increase in the H^+ concentration. A strong reduction in rate is indeed observed, but the values of the rate constants in Table III are still by far too large. A specific catalytic effect must therefore be present, and possibly the reduction in the rate constants with increasing H^+ concentration can be due to the fact that the catalytic reaction is of lower order with respect to the H^+ concentration.

(25) A. R. Olson and T. R. Simonson, J. Chem. Phys., 17, 1167 (1949).

(26) J. Faucherre, Compt. rend., 227, 1367 (1958).