One can calculate the spin density on the metals by squaring the t_{2g} MO's and obtaining the Mulliken overlap population.[22] The fact that reasonable spin densities (Table II) are obtained from the t_{2g} MO coefficients indicates that this calculation has properly estimated the per cent of Cl p_π bonding in the $IrCl_6^{2-}$ case. The general trend of increased ligand participation in the t_{2g} MO across the series (Table II) could be verified in the future with esr studies on the $ReCl_6^{2-}$ and $OsCl_6^{2-}$ complexes.

Nuclear Quadrupole Resonance (nqr) Coupling Constants (*eqQ*).—In nuclear quadrupole resonance one measures transitions between nuclear spin states which are split by the interaction of nuclear states with the electric field gradient produced by the electrons. Consequently, the electron distribution in well-defined atomic and molecular systems containing quadrupolar nuclei can be measured. Because the resonance frequency is dependent upon the local electronic environment of the nucleus, nqr, like esr, sometimes affords the only feasible physical method for the elucidation of electronic structure.

The interpretation of nqr spectra of halide ions has always been done in terms of a valence bond approach (the well-known Townes–Dailey treatment[23]), but for complexes in particular, and other compounds as well, a molecular orbital treatment is far more useful since it ties in directly with the general picture of electronic structures of complexes and with the results of other kinds of measurements (*e.g.*, esr, nmr) and is more flexible. A relationship between MO eigenvectors and *eqQ* values has been developed[4] and will be applied to the molecules treated in this paper.

Using eq 11 of ref 4, the nqr relationships[24] between Cl p_σ and p_π electrons, the eigenfunctions or MO coefficients,[14] and the overlap integrals,[14] we have calculated the nqr coupling constants, *eqQ*, tabulated in Table II.

The excellent agreement between calculated and observed *eqQ* values substantiates our belief that the MO method employed here gives reasonable predictions and explanations of the bonding properties in these complexes. As will be discussed elsewhere, had a free-ion degree of orbital energy dependence on charge been used, the calculated metal charge would have been much lower, the degree of M–Cl covalence much higher, and, thus, the *eqQ* values much higher than the experimental ones. Furthermore, the increase in *eqQ* across the series verifies the contention that the effective metal charge decreases across the series *via* electron donation through the Cl $3p_\sigma$ orbitals.

The occupation of the Cl orbitals is also given in Table II. Note the decrease in the number of Cl $3p_\sigma$ electrons across the series. The Cl 3s occupation stays constant, presumably because (1) the Cl 3s orbital energy is quite low with respect to that of the 3p, and (2) the Cl 3s radial wave function is less diffuse than the 3p wave function.

[22] R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833, 1841 (1955).
[23] C. H. Townes and B. P. Dailey, *ibid.*, **17**, 782 (1949).
[24] T. P. Das and E. L. Hahn, "Nuclear Quadrupole Resonance Spectroscopy," Academic Press Inc., New York, N. Y., 1958.

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Kinetic Study on the Alkaline Hydrolysis of $Co(NH_3)_5O_2C_2Cl_3^{2+}$ and $Co(NH_3)_5O_2C_2Cl_2H^{2+}$

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The rates of hydrolysis in alkaline solution of $(NH_3)_5CoO_2C_2Cl_2H^{2+}$ and $(NH_3)_5CoO_2C_2Cl_3^{2+}$ were found to follow the general rate law $-d \ln [\text{complex}]/dt = k_1[OH^-] + k_2[OH^-]^2$. At 25° and $\mu = 1.0$ (NaCl), for the dichloroacetato complex $\Delta H_1^{\ddagger}$ and $\Delta S_1^{\ddagger}$ are 28.9 kcal mole^{-1} and 28.8 cal mole^{-1} deg^{-1}; and $\Delta H_2^{\ddagger}$ and $\Delta S_2^{\ddagger}$ are 20.8 kcal mole^{-1} and 0.3 cal mole^{-1} deg^{-1}. For the trichloroacetato complex $\Delta H_1^{\ddagger}$ and $\Delta S_1^{\ddagger}$ are 23.3 kcal mole^{-1} and 12.5 kcal mole^{-1} deg^{-1}; $\Delta H_2^{\ddagger}$ and $\Delta S_2^{\ddagger}$ are 22.3 kcal mole^{-1} and 8.5 cal mole^{-1} deg^{-1}. The values for k_1 verify trends predicted for an SN1CB mechanism. The results are discussed with relation to acid hydrolysis of these complexes and the hydrolysis of the organic esters.

Introduction

Although the alkaline hydrolysis of both $Co(NH_3)_5O_2C_2Cl_2H^{2+}$ and $Co(NH_3)_5O_2C_2Cl_3^{2+}$ have already been studied,[1] recent work on $Co(NH_3)_5O_2C_2F_3^{2+}$ has revealed a term in the rate law second order in hydroxide ion.[2] This path proceeds with O–C bond breaking. The present study was undertaken to determine the effect of changing the carboxylate ligand on this $k_2 \cdot [OH^-]^2$ path. The results also determine whether the formerly observed trend[1] in rates for these complexes is due to an enthalpy or entropy of activation effect.

Experimental Section

Preparation and Analysis of Complex Salts.—Both the dichloroacetato and trichloroacetato complexes were prepared by

[1] F. Basolo, J. G. Bergman, and R. G. Pearson, *J. Phys. Chem.*, **56**, 22 (1952).
[2] R. B. Jordan and H. Taube, *J. Am. Chem. Soc.*, **88**, 4406 (1966).

heating an aqueous solution containing a tenfold molar excess of the carboxylic acid and $[(NH_3)_5CoOH_2](ClO_4)_3$ at 70° for 2 hr. The crude product, collected on cooling, was recrystallized by dissolving in a minimum of water at room temperature and adding concentrated perchloric acid to give a solution 1 *M* in $HClO_4$. The product was washed with cold water and methanol and dried under vacuum.

The product was analyzed for perchlorate by titrating the hydrogen ion eluted from an ion-exchange column (Dowex-8 H^+ form) by a known weight of the complex. Extinction coefficients were compared to those previously reported:[3] $[(NH_3)_5CoO_2C_2Cl_2H](ClO_4)_2$: for 42.1% ClO_4^- found and 42.0% calculated, ϵ is 72.8 (71.0[3]) at 502 mμ; 58.3 (56.4[3]) at 350 mμ. $[(NH_3)_5CoO_2C_2Cl_3](ClO_4)_2$: for 39.0% ClO_4^- found and 39.2% calculated, ϵ is 77.0 (77.9[3]) at 505 mμ; 55.5 (57.1[3]) at 350 mμ.

Kinetic Measurements.—Reagent grade NaOH and NaCl (Baker and Adamson) were used as supplied. Carbonate-free NaOH solutions were prepared in the standard way by diluting 50% NaOH solutions. All solutions were made up in water redistilled from alkaline permanganate.

Spectral measurements were made on a Bausch and Lomb Spectronic 505 spectrophotometer. Temperature was controlled to ±0.10°. Runs below 15° were carried out with the thermostated bath in a cold room at 0°.

The general procedure employed was to preequilibrate a solution of the complex in 1 *M* NaCl, in a volumetric flask, and a solution of 1.00 *M* NaOH at the temperature desired. The solution of complex was then diluted to volume in the volumetric flask with the sodium hydroxide. The resulting solution was shaken, aliquots were withdrawn at various times and quenched in excess 1 *M* $HClO_4$ diluted to a known volume, and the absorbance was recorded at some predetermined wavelength. In some cases, when reactions were too fast to permit the use of pipets, sodium hydroxide was added from a syringe and samples were taken with a syringe.

A major source of harassment in these studies was the formation of cobaltic oxide due to decomposition of the hydrolysis products. The hydrolysis of the trichloroacetato complex was sufficiently fast that the reaction could be followed for up to 2 half-lives without interference from this decomposition.

For the dichloroacetato complex there is only about 10% decomposition after 90% hydrolysis but the finely divided precipitate interfered with the absorbance measurements. The precipitate was removed from the acid-quenched aliquots by filtration through a 0.45-μ Millipore filter (Millipore Filter Corp., Bedford, Mass.).

In all cases the infinite time absorbance was determined from the spectrum of $(NH_3)_5CoOH_2^{3+}$ in the same ionic medium as samples from the kinetic run. Because of the low extinction coefficient of the product at the wavelengths used, correction of the infinite time absorbance for up to 15% decomposition has no significant effect on the calculated rate constants.

Reactions were run at an ionic strength of 1.0 *M* adjusted with NaCl. Hydroxide ion was always in at least tenfold excess over complex ion concentration so that rates were always pseudo first order in OH^-. All reactions were run in volumetric flasks wrapped with aluminum foil.

For $(NH_3)_5CoO_2C_2Cl_3^{2+}$ the absorbance changes were followed at 280 mμ; for $(NH_3)_5CoO_2C_2Cl_2H^{2+}$, at 288 m$\mu$.

Results

From the study of the variation of hydrolysis rate with hydroxide ion concentration, at constant ionic strength $\mu = 1.0$ (NaCl), the rate law for both complexes studied was found to be

$$\frac{-\mathrm{d}\ln[\text{complex}]}{\mathrm{d}t} = k_{\text{obsd}} = k_1[\text{OH}]^- + k_2[\text{OH}^-]^2$$

A plot of $k_{\text{obsd}}/[OH^-]$ *vs.* $[OH^-]$ gives a straight line with slope k_2 and intercept k_1.

Table I gives experimental values of $k_{\text{obsd}}/[OH^-]$ for the hydrolysis of $(NH_3)_5CoO_2C_2Cl_2H^{2+}$ and values of $k_{\text{obsd}}/[OH^-]$ calculated on the basis of the best fit of the experimental data to the above rate law. Table II gives the analogous data for the hydrolysis of $(NH_3)_5CoO_2C_2Cl_3^{2+}$.

TABLE I

RATES OF HYDROLYSIS OF $(NH_3)_5CoO_2C_2Cl_2H^{2+}$

Temp, °C	$[OH^-]$, *M*	$10^3(k_{\text{obsd}}/[OH^-])$, M^{-1} sec^{-1} Obsd	Calcd[a]
10.8	0.10	0.755	0.730
	0.40	0.862	0.868
	0.70	1.01	0.988
	1.00	1.15	1.15
15.2	0.10	1.31	1.31
	0.40	1.51	1.52
	0.70	1.74	1.74
	1.0	1.92	1.94
25.0	0.10	6.08	6.09
	0.30	6.53	6.67
	0.50	7.45	7.25
	0.82	8.10	8.25
35.2	0.10	30.4	28.5
	0.30	33.0	30.2
	0.50	32.2	31.9

[a] Calculated from values of k_1 and k_2 in Table III.

TABLE II

RATES OF HYDROLYSIS OF $(NH_3)_5CoO_2C_2Cl_3^{2+}$

Temp, °C	$[OH^-]$, *M*	$10^3(k_{\text{obsd}}/[OH^-])$, M^{-1} sec^{-1} Obsd	Calcd
5.0	0.099	1.26	1.27
	0.197	1.55	1.55
	0.257	1.72	1.71
	0.300	1.83	1.83
	0.395	2.10	2.10
16.0	0.059	5.29	5.24
	0.136	6.16	6.12
	0.155	6.36	6.34
	0.195	6.81	6.79
	0.255	7.53	7.48
	0.292	7.95	7.89
25.4	0.064	25.0	25.1
	0.083	25.9	26.0
	0.097	26.5	26.5
	0.136	28.3	28.4
	0.195	30.8	31.0
	0.292	35.2	35.4

The best values of k_1 and k_2 and the values of $\Delta H_1^{\ddagger}$ and $\Delta H_2^{\ddagger}$ are given in Tables III and IV for the dichloroacetato and trichloroacetateo complexes, respectively. The values of $\Delta H^{\ddagger}$ were determined from plots of $\ln k_1/T$ and $\ln k_2/T$ *vs.* $1/T$, and $\Delta S^{\ddagger}$ was calculated from the transition state theory equation.

TABLE III

RATE CONSTANTS AND ACTIVATION PARAMETERS FOR THE HYDROLYSIS OF $(NH_3)_5CoO_2C_2Cl_2H^{2+}$

Temp, °C	10^3k_1, M^{-1} sec^{-1}	10^3k_2, M^{-1} sec^{-1}
10.8	0.68	0.47
15.2	1.24	0.71
25.0	5.80	2.9
35.2	27.6[a]	8.5[a]
$\Delta H^{\ddagger}$, kcal mole^{-1}	28.9	20.8
$\Delta S^{\ddagger}$, cal mole^{-1} deg^{-1}	28.8	0.3

[a] Calculated from extrapolation of ln (k/T) *vs.* $1/T$ plot.

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(3) K. Kuroda and P. S. Gentile, *Bull. Chem. Soc. Japan*, **38**, 1362 (1965).

TABLE IV

RATE CONSTANTS AND ACTIVATION PARAMETERS FOR THE HYDROLYSIS OF $(NH_3)_5CoO_2C_2Cl_3^{2+}$

Temp, °C	10^3k_1, M^{-1} sec^{-1}	10^3k_2, M^{-1} sec^{-1}
5.0	1.00	2.77
16.0	4.57	11.5
25.4	22.2	45.2
$\Delta H^{\ddagger}$, kcal mole^{-1}	23.3	22.3
$\Delta S^{\ddagger}$, cal mole^{-1} deg^{-1}	12.5	8.5

Discussion

The previous study[2] of the alkaline hydrolysis of $(NH_3)_5CoO_2C_2F_3^{2+}$ has shown that the hydrolysis proceeds by a rate law similar to that found here. Oxygen-18 tracer studies on $(NH_3)_5CoO_2C_2F_3^{2+}$ have shown that the $k_1[OH^-]$ path involves Co–O bond breaking, and the $k_2[OH^-]^2$ path, O–C bond breaking. It is assumed that the same general mechanism is being followed by the dichloroacetato and trichloroacetato complexes; that is, the $k_1[OH^-]$ path presumably follows the normal SN1CB mechanism

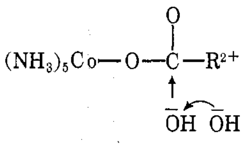
$$Co(NH_3)_5O_2CR^{2+} + OH^- \rightleftharpoons Co(NH_3)_4NH_2O_2CR^+ + H_2O$$

$$H_2O + Co(NH_3)_4NH_2O_2CR^+ \longrightarrow Co(NH_3)_4NH_2OH_2^{2+} + RCO_2^-$$

$$Co(NH_3)_4NH_2OH_2^{2+} \longrightarrow Co(NH_3)_5OH^{2+}$$

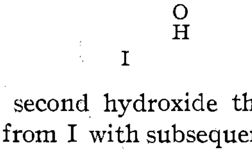
$$(R = CCl_3 \text{ or } CCl_2H_2)$$

A possible mechanism proposed for the $k_2[OH^-]^2$ path[2] involves attack of an OH^- on the carbonyl carbon followed by a second OH^- removing a proton from the first



$$(NH_3)_5Co{-}O{-}\overset{\displaystyle O}{\underset{\displaystyle \uparrow \atop \bar{O}H\ \bar{O}H}{C}}{-}R^{2+}$$

In the case of the trifluoroacetato complex the low activation energy for this path (6.8 kcal mole^{-1}) only seems consistent with a concerted mechanism with considerable bond making in the activated complex. The results on the chloroacetato complexes presented here could be interpreted on the basis of the same mechanism. However, the activation energies for the latter complex do not require a concerted mechanism, and an intermediate (I) may form by reaction with one



$$(NH_3)_5CO{-}O{-}\overset{\displaystyle \bar{O}}{\underset{\displaystyle OH}{C}}{-}R^+$$

I

hydroxide. The second hydroxide then removes the hydroxyl proton from I with subsequent decomposition to products.

The tracer results of Bunton and Llewellyn[4] support the assumption that the $k_2[OH^-]^2$ path in the choroacetato complexes is analogous to that in the trifluoroacetato complex. These results show approximately 15 and 8% solvent oxygen incorporated into the carboxylate anion product for the trichloroacetato and dichloroacetato complexes, respectively. This tracer study was carried out at equivalent concentrations of complex and hydroxide ion equal to 0.20 M. For this condition it is possible to calculate the amount of product formed from O–C bond breaking

$$[RCO^{18}O^-] = 0.20 - \frac{k_1}{k_2}\ln\left(1 + \frac{k_2}{k_1}(0.20)\right)$$

Assuming that the ratio k_1/k_2 does not change with ionic strength, at 25° the results are 17% $Cl_3CO^{18}O^-$ and 5% $Cl_2HCO^{18}O^-$. Since there are two oxygens in the carboxylate ion product of which only one can be derived from solvent, this gives 8.5 and 2.5% solvent oxygen in the products, respectively. The higher values found by Bunton and Llewellyn may be due to oxygen exchange during hydrolysis (as found in $Co(NH_3)_5O_2C_2F_3^{2+}$). It can be concluded that the rate study and the previous tracer study are consistent with a hydrolysis mechanism analogous to that found for $(NH_3)_5CoO_2C_2F_3^{2+}$.

If the mechanism of hydrolysis by the $k_1[OH^-]$ path is SN1CB, then the rate-controlling process is breaking of the Co–ligand bond. For a series of carboxylic acid ligands it would be expected that this bond strength would decrease with increasing pK_a of the acid. Thus the values of $\Delta H_1^{\ddagger}$ of 22, 23.3, and 28.9 kcal mole^{-1} for the $O_2C_2F_3$, $O_2C_2Cl_3$, and $O_2C_2Cl_2H$ complexes, respectively, are consistent with the predicted trend. A similar argument was used by Basolo, *et al.*,[1] to explain the relative rates of hydrolysis of these complexes. However, it was not known previously whether the rate differences were due primarily to enthalpy or entropy of activation effects.

It is also useful to compare the activation parameters for the base hydrolysis and uncatalyzed aquation of these complexes. If the rate-controlling step in the aquation is also metal–ligand bond breaking then the enthalpies of activation for alkaline hydrolysis and aquation would be expected to show the same trends. However, as shown in Table V, the activation enthalpies for aquation are almost the same for the series of chloroacetate and the trifluoroacetate complexes. Monacelli, *et al.*,[5] have argued that because of the similarity in rates and activation parameters for the aquation of pentaamminetrifluoroacetatocobalt(III), -rhodium(III), and -iridium(III), this process proceeds with C–O bond breaking. The tracer results of Bunton and Llewellyn[4] show that Co–O bond breaking occurs during the aquation of the acetatopentaamminecobalt(III). The activation parameters listed in Table V do not show any trend indicative of any such dual mechanism. Also it does not seem reasonable, on the basis of the base-catalyzed hydrolysis results, to suppose that both Co–O and O–C bond breaking would have the same values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ throughout the series. For example, both Co–O and O–C bond break-

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[4] C. A. Bunton and D. R. Llewellyn, *J. Chem. Soc.*, 1692 (1953).

[5] F. Monacelli, F. Basolo, and R. G. Pearson, *J. Inorg. Nucl. Chem.*, **24**, 1241 (1962).

TABLE V

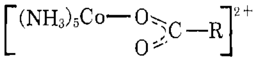
RATES OF UNCATALYZED ACID HYDROLYSIS

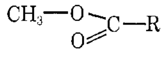
Complex	$\Delta H^{\ddagger}$, kcal mole^{-1}	$\Delta S^{\ddagger}$, eu	Ref
$Co(NH_3)_5O_2C_2ClH_2$	26.3	−1.6	*a*
$Co(NH_3)_5O_2C_2Cl_2H$	26.4	−3.5	*a*
$Co(NH_3)_5O_2C_2Cl_3$	25.7	−3.0	*a*
$Co(NH_3)_5O_2C_2CF_3$	26	−2	*b*

[a] K. Kuroda, *Nippon Kagaku Zasshi*, **82**, 572 (1961). [b] F. Monacelli, F. Basolo, and R. G. Pearson, *J. Inorg. Nucl. Chem.*, **24,** 1241 (1962).

ing have lower activation enthalpies for the trifluoroacetato than for the dichloroacetato complex. Therefore, the $\Delta H^{\ddagger}$ for aquation of the latter complex should be higher whichever mechanism is operative. The conclusion is that the acid hydrolysis of these complexes is probably proceeding with both bond making and breaking in the transition state. The exact degree is still open to speculation.[6,7]

It would be interesting to determine the effect of the metal atom on reactivity by comparing the hydrolysis behavior of the inorganic complexes and the organic esters. Because of the differences in mechanism between the two systems, a quantitative comparison is not possible. However, the differences in mechanism do indicate the effect of the metal atom. The O–C bond breaking by a path first order in hydroxide ion occurs very little, if at all, in the inorganic complex, possibly owing to the increased double-bond character of this bond in the complex as compared to the organic ester.





For the trifluoroacetato complex this effect would be greatest and therefore O–C bond breaking would be less favorable. However, there is the competing inductive effect making it easier for an OH^- to attack the acyl carbon. These two effects can be used to rationalize the rate parameters found for the carboxylatopentaamminecobalt(III) complexes.

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(6) C. H. Langford, *Inorg. Chem.*, **4**, 265 (1965).

(7) M. L. Tobe, *Record Chem. Progr.* (Kresge-Hooker Sci. Lib.), **27**, 79 (1966).

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Kinetics and Mechanisms of Reactions of Gold(III) Complexes. I. The Equilibrium Hydrolysis of Tetrachlorogold(III) in Acid Medium

BY WILLIAM ROBB

Received October 24, 1966

The tetrachlorogold(III) anion reacts with water and establishes itself in equilibrium with other chlorogold(III) species as

$$AuCl_4^- + H_2O \underset{k_2}{\overset{k_1}{\rightleftharpoons}} AuCl_3(H_2O) + Cl^-$$

$$AuCl_3(H_2O) \overset{K_a}{\rightleftharpoons} AuCl_3(OH)^- + H^+$$

$$AuCl_3(OH)^- + H_2O \underset{k_4}{\overset{k_3}{\rightleftharpoons}} AuCl_2(H_2O)(OH) + Cl^-$$

At 25° values of $k_1 = 2.2 \times 10^{-2}$ sec^{-1}, $k_2/K_a = 9.3 \times 10^3\ M^{-2}$ sec^{-1}, $k_3 = 3.3 \times 10^{-4}$ sec^{-1}, and $k_4 = 8.3 \times 10^{-2}\ M^{-1}$ sec^{-1} were obtained. The activation parameters were found to be: $\Delta H_1^{\ddagger} = 15.5$, $\Delta H_2^{\ddagger} = 9.1$, $\Delta H_3^{\ddagger} = 26.9$, and $\Delta H_4^{\ddagger} = 15.4$ kcal/mole; $\Delta S_1^{\ddagger} = -15.5$, $\Delta S_2^{\ddagger} = -25$, $\Delta S_3^{\ddagger} = 14$, and $\Delta S_4^{\ddagger} = -13$ eu. The value for K_a is $\sim 10^{-3}\ M$.

Introduction

A perusal of the literature reveals that no more than four studies on the rates and mechanism of reactions in the gold(III) system have been reported. These are the now well-known chloride ligand exchange reactions of tetrachlorogold(III) by Rich and Taube,[1] the polarographic study of Beran and Vlček[2] on the formation of the ethylenediaminedichlorogold(III) complex from $AuCl_4^-$ in acid medium, the studies in the diethylenetriaminehalogold(III) system by Baddley and Basolo,[3] and, finally, the recent report on the hydrolysis of $AuCl_4^-$ by Kazakov.[4]

Gold(III) and platinum(II) are isoelectronic, they both form square-planar complexes, and they behave similarly[5] from a mechanistic viewpoint, but they have very dissimilar rates. Thus $[Au(dien)Cl]^{2+}$ reacts

(1) R. L. Rich and H. Taube, *J. Phys. Chem.*, **58**, 1 (1954).

(2) P. Beran and A. A. Vlček, *Collection Czech. Chem. Commun.*, **24**, 3572 (1959).

(3) W. H. Baddley and F. Basolo, *Inorg. Chem.*, **3**, 1087 (1964).

(4) V. P. Kazakov, *Zh. Neorgan. Khim.*, **10**, 1276 (1965).

(5) F. Basolo, Symposium on Mechanisms of Inorganic Reactions, Lawrence, Kansas, June 1964.