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Steric Effects in the Copper(II) Chelates of 2-Pyridyl Alcohols

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The acid dissociation constants of 2-pyridylcarbinol, 6-methyl-2-pyridylcarbinol, 2-(β-hydroxyethyl)pyridine, and 2-(β-hydroxyethyl)-6-methylpyridine and the stability constants of the Cu(II) chelates of these ligands have been determined by the Calvin–Bjerrum potentiometric titration technique in 50 vol. % 1,4-dioxane–water at 0, 15, and 25°. Enthalpy values were determined from direct calorimetric measurements as well as from the temperature dependence of the formation constants. The results of the study show (1) the presence of the methyl group in the 6-position decreases enthalpy and increases entropy, and (2) the increase in entropy is not large enough to counteract the effects of steric hindrance.

Introduction

The factors affecting the stability of metal chelates have been investigated extensively by various workers and it has been established that a definite relationship exists between the basic strength of different types of ligands and their affinity for metal ions. Bjerrum[2] has pointed out that the ratio log K_{av}/pK_{NH} is constant for the same metal with a series of closely related ligands except when steric hindrance causes a decrease in stability. A lowering in the above ratio has thus been interpreted as indicative of steric hindrance. However, in order to have a more complete understanding of the process of chelation, it is desirable to study the changes in free energy ($\Delta F°$), enthalpy ($\Delta H°$), and entropy ($\Delta S°$) of formation of the chelates. In the present study $\Delta H°$ values for the copper(II) chelates of certain 2-pyridyl alcohols were determined both directly from calorimetric measurements and from the temperature dependence of the formation constants. Results obtained using both methods are included for comparative purposes.

Experimental

Materials.—2-Pyridylcarbinol, 6-methyl-2-pyridylcarbinol, 2-(β-hydroxyethyl)pyridine, and 2-(β-hydroxyethyl)-6-methylpyridine were obtained from Aldrich Chemical Company, Milwaukee, Wisconsin, and purified before use by repeated distillation *in vacuo*. The purity of the samples was established by elemental analysis as well as by the agreement of their boiling points with those reported in the literature.

Fisher reagent grade 0.1 *N* carbonate-free sodium hydroxide solution was standardized against reagent grade potassium acid phthalate. Approximately 0.01 *N* perchloric acid solution was prepared from a 60% solution of the acid (Allied Chemical) and was standardized against the sodium hydroxide by potentiometric titration. Stock solutions of Cu(II) ion were prepared from copper perchlorate and copper nitrate, and the strength of the solutions was determined by electrodeposition and titration with EDTA using pyrocatechol violet as an indicator. The dioxane used as solvent was obtained from Fisher Scientific and was purified according to the method outlined by Vogel,[3] kept over sodium, and distilled as needed.

Potentiometric Apparatus, Procedures, and Calculations.—The stability constants were determined at 0, 15, and 25° by the Bjerrum method[4] of potentiometric titration in 50 vol. % 1,4-dioxane–water. The titration apparatus is essentially the same as that described by Freiser, *et al.*[5]

The titration procedure has been previously described.[6] The true volumes of the solutions were obtained by multiplying the calculated total volume obtained by: 0.958 at 0°, 0.971 at 15°, and 0.979 at 25°. A Radiometer 4 pH meter was used to make pH measurements, providing for a reading accuracy within ±0.001 pH unit and 0.1 mvolt. Radiometer glass electrode B, which covers the full pH range (0–14) and has a maximum salt error of ±0.01 pH unit above pH 13, was used. The corrections to be applied to the glass electrode were determined in a manner similar to that described by Van Uitert[7] and Charles.[8] The factors added to all pH readings made in this study were: +0.01 at 0°, +0.04 at 15°, and +0.07 at 25°. By using an excess of ligand concentration (8:1), the pH range of chelate formation was lowered and the hydrolysis region of Cu(II) (pH 6) was avoided. In the case of 6-methyl-2-pyridylcarbinol, 2-(β-hydroxyethyl)pyridine, and 2-(β-hydroxyethyl)-6-methylpyridine, the log K_2 values were obtained from extrapolated $\bar{n}$ values.

The acid dissociation constants were determined by titrating a mixture of the ligand and perchloric acid with standard sodium hydroxide. Since the acidities of the cationic acid and of the alcoholic hydroxyl group are sufficiently different, their acid dissociation constants can be defined by the equations

$$K_{NH} = \frac{[H^+][RH]}{[RH_2^+]} \quad K_{OH} = \frac{[H^+][R^-]}{[RH]}$$

The terms $[H^+]$, $[RH]$, $[RH_2^+]$, and $[R^-]$ represent the concentrations of the hydrogen ion, the unprotonated ligand, the protonated reagent, and the reagent anion, respectively.

The stepwise constants for the formation of a 1:1 and of a 1:2 chelate may be expressed as

$$K_1 = \frac{[MR^+]}{[M^{+2}][R^-]} \quad K_2 = \frac{[MR_2]}{[MR^+][R^-]}$$

where $[M^{+2}]$ is the metal ion concentration and $[R^-]$ is the concentration of the chelate anion while $[MR^+]$ and $[MR_2]$ refer to the concentrations of the 1:1 and 1:2 chelates, respectively.

The equilibrium constants are concentration quotients obtained in dilute solutions, approximately 5×10^{-4} *M* in metal ion, using a metal:ligand ratio of 1:8.

The formation constants were obtained from plots of $\bar{n}$ *vs.* pR^- using the method of Freiser, *et al.*[5] The values of pR^- at $\bar{n}$ = 0.5, 1.0, and 1.5 were taken as equal to log K_1, log K_{av},

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[2] J. Bjerrum, *Chem. Rev.*, **46**, 381 (1950).

[3] A. I. Vogel, "A Textbook of Practical Organic Chemistry," Longmans, Green and Co., New York, N. Y., 1948, p. 195.

[4] J. Bjerrum, "Metal-Amine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1941.

[5] H. Freiser, R. G. Charles, and W. D. Johnston, *J. Am. Chem. Soc.*, **74**, 1383 (1952).

[6] M. Calvin and K. W. Wilson, *ibid.*, **67**, 2003 (1945).

[7] L. G. Van Uitert and C. G. Haas, *ibid.*, **75**, 451 (1953).

[8] R. G. Charles, Ph.D. Thesis, University of Pittsburgh, 1952.

TABLE I

STABILITY DATA FOR THE CHELATION OF 2-PYRIDYL ALCOHOLS WITH Cu(II) IN 50 VOL. % DIOXANE–WATER

	Temp., °C.	pK_{NH}	pK_{OH}	$\log K_1$	$\log K_2$	$2 \log K_{av}$
2-Pyridylcarbinol	0	4.18	13.68	10.45	9.57	20.13
	15	4.19	13.14	10.22	9.14	19.51
	25	4.16	12.90	10.19	8.92	19.15
6-Methyl-2-pyridylcarbinol	0	4.94	13.77	10.13	9.18	19.13
	15	4.71	13.14	9.71	8.76	18.59
	25	4.56	12.83	9.81	8.56	18.35
2-(β-Hydroxyethyl)pyridine	0	4.73	13.55	10.12	9.18	19.39
	15	4.65	13.11	9.63	8.82	18.75
	25	4.52	12.75	9.52	8.52	18.54
2-(β-Hydroxyethyl)-6-methylpyridine	0	5.58	13.86	9.44	9.12	18.84
	15	5.32	13.20	9.36	9.10	18.39
	25	5.14	12.81	9.34	8.88	18.12

TABLE II

THERMODYNAMIC DATA FOR THE FORMATION OF Cu(II) 2-PYRIDYL ALCOHOLS

		Calorimetric method			Temp. coeff. method[c]	
Ligand	$-\Delta F^{\circ}$[a]	Δt[d]	$-\Delta H^{\circ}$[a]	ΔS°[b]	$-\Delta H^{\circ}$[a]	ΔS°[b]
2-Pyridylcarbinol	26.13	0.417	23.32	9.4	14.59	38.7
		0.213[e]	23.81[e]	7.8[e]		
6-Methyl-2-pyridylcarbinol	25.04	0.302	13.53[f]	38.6	14.52	35.3
		0.149[e]	13.28[e,f]	39.4[e]		
2-(β-Hydroxyethyl)pyridine	25.30	0.296	13.82	38.5	13.65	39.1
2-(β-Hydroxyethyl)-6-methylpyridine	24.72	0.283	12.43	41.2	12.20	42.0

[a] Kcal./mole at 25°. [b] Cal./deg. [c] ΔH° values estimated from graphical results at 0, 15, and 25°. [d] °C. [e] Values obtained using 2.47×10^{-3} mole of $Cu(NO_3)_2$. [f] Heat of precipitation.

and $\log K_2$, respectively. This is based on the assumption that at $\bar{n} = 0.5$ the species MR_2 is of negligible concentration and that M^{+2} is negligible at $\bar{n} = 1.5$. The values of $\log K_1$ and $\log K_2$ (Table I) could be corrected using the convergence equations of Verhoek[9] as applied by Van Uitert,[10] but this was not done since the thermodynamic data have been obtained using the values of $2 \log K_{av}$ which are not altered by these corrections.

Calorimetric Apparatus, Procedure, and Calculations.—The calorimetric measurements were made with a dewar-type apparatus (Cenco No. 78044) consisting of a jacketed container with cover into which a glass calorimeter of approximately 500-ml. capacity is fitted. The insulated cover has openings for a stirrer (fashioned from 2-mm. capillary tubing), a sample holder, and a Beckmann thermometer and was modified to provide openings for glass tubes leading to and from the constant temperature bath by which both the water in the jacket and the contents of the calorimeter were maintained at a temperature of 25.0 ± 0.1°. The heat capacity of this calorimeter was determined by neutralizing exactly 5 ml. of 2 *N* sodium hydroxide with sulfuric acid for which reaction the heat evolved was reported to be 165 cal. at 25°.[11] The value for the heat capacity of the calorimeter thus obtained is 49.5 cal.

For each measurement, exactly 5 ml. of aqueous solution containing 4.94×10^{-3} mole of $Cu(NO_3)_2$ was introduced into the sample holder, which previously had been plugged with paraffin. Sufficient ligand (a slight excess) to form a 1:2 chelate was placed in the calorimeter vessel, and to obtain the anionic form of the ligand this was neutralized with standard 0.1 *N* sodium hydroxide. This solution was diluted to 250 ml. with water followed by the addition of 255 ml. of pure dioxane. Distilled water, which was passed through a column containing ion-exchange resins IR-200 and IRA-400 in the ratio 1:4, was used for all reactions. After a suitable interval of time for temperature equilibration the metal solution was mixed with the ligand anion and the increase in temperature was noted every 15 sec. The temperature increase for the reaction (Table II) was then calculated using standard methods.[12]

From the increase in temperature (Δt), the heat of reaction for the formation of the 1:2 copper(II) chelate (ΔH) was calculated using the equation

$$n(\Delta H) = mc\Delta t + m_1c_1\Delta t + C_{cal}\Delta t - n\Delta H_{diln}$$

where n is the number of moles of the chelate formed, m the mass of aqueous solution, m_1 the mass of dioxane, c the specific heat of water, c_1 the specific heat of dioxane (0.42 at 25°),[13] C_{cal} the heat capacity of the calorimeter, and ΔH_{diln} the heat of dilution for cupric ion in 50 vol. % dioxane–water. The value for ΔH_{diln} determined in a separate experiment using 5 ml. of solution containing 4.94×10^{-3} mole of $Cu(NO_3)_2$ is 12.3 kcal./mole. The additivity of the heat capacities of water and dioxane has been demonstrated by Kido and Fernelius.[14]

The ΔH values calculated by this method must be corrected for hydrolysis of the ligand anion prior to the addition of the cupric ion. Accordingly, each ΔH of neutralization was determined directly by allowing the sodium salt of the ligand in solution to react with perchloric acid. The values obtained are 9.36, 8.56, 10.45, and 10.09 kcal./mole for 2-pyridylcarbinol, 6-methyl-2-pyridylcarbinol, 2-(β-hydroxyethyl)pyridine, and 2-(β-hydroxyethyl)-6-methylpyridine, respectively, in 50 vol. % dioxane–water. From the pK_{OH} values at 25° (Table I) the per cent hydrolysis of each ligand anion was calculated. Based on the percentage of hydrolysis and on the ΔH of neutralization values, corrections of +1.45 (2-pyridylcarbinol), +1.24 (6-methyl-2-pyridylcarbinol), +1.39 (2-(β-hydroxyethyl)pyridine), and +1.45 kcal./mole (2-(β-hydroxyethyl)-6-methylpyridine) were applied to the ΔH values obtained for the chelation reactions.[15] The average corrected values for ΔH are listed in

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[9] F. H. Verhoek, *J. Am. Chem. Soc.*, **67**, 1334 (1945).

[10] L. G. Van Uitert, W. C. Fernelius, and B. E. Douglas, *ibid.*, **75**, 457 (1953).

[11] F. D. Rossini, *et al.*, "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards Circular 500 (1952).

[12] J. M. Sturtevant in A. Weissberger, "Physical Methods of Organic Chemistry," Part I, Vol. I, Interscience Publishers, New York, N. Y., 1959, p. 541.

[13] W. Herz and L. Lorenz, *Z. physik. Chem.*, **140A**, 406 (1929).

[14] H. Kido and W. C. Fernelius, *J. Phys. Chem.*, **65**, 574 (1961).

[15] For determinations using 2.47×10^{-3} mole of $Cu(NO_3)_2$, the corrections applied were 1.99 kcal./mole for 2-pyridylcarbinol and 1.67 kcal./mole for 6-methyl-2-pyridylcarbinol.

Table II. Values for individual runs, at least three for each compound, were within 2% of the listed data. For the complete calorimetric data see Table III.

TABLE III

CALORIMETRIC DATA

Ligand, g.	M^{+2}, moles × 10^{-3}	Wt. aq. soln., g.[a]	Δt_{cor}[b]	$-\Delta H_{uncor}$[c]	$-\Delta H_{cor}$[d]
		2-Pyridylcarbinol			
1.1583	4.941	243.6	0.416	34.06	23.21
1.1044	4.941	243.5	0.419	34.28	23.43
1.1464	4.941	243.5	0.418	34.21	23.37
0.5675	2.471	242.7	0.212	34.67	23.81
0.5508	2.471	242.7	0.212	34.67	23.81
0.5706	2.471	243.0	0.213	34.74	23.90
		6-Methyl-2-pyridylcarbinol			
1.2993	4.941	244.4	0.301	24.70	13.65
1.2989	4.941	244.5	0.299	24.51	13.45
1.2990	4.941	244.5	0.300	24.57	13.52
0.6520	2.471	243.3	0.149	24.44	13.29
0.6721	2.471	243.4	0.149	24.42	13.45
		2-(β-Hydroxyethyl)pyridine			
1.3147	4.941	244.5	0.301	24.69	13.79
1.3425	4.491	244.5	0.302	24.75	13.84
1.3379	4.941	244.4	0.301	24.70	13.80
		2-(β-Hydroxyethyl)-6-methylpyridine			
1.4450	4.941	244.4	0.282	23.17	12.27
1.3756	4.941	244.5	0.285	23.38	12.53
1.4079	4.941	244.5	0.286	23.47	12.63

[a] Weight of dioxane used was 266.6 g. [b] Δt_{cor} is the increase in temperature during the reaction after correction according to ref. 12. [c] $-\Delta H_{uncor} = \Delta H_{rxn}$. [d] $-\Delta H_{cor} = \Delta H_{rxn} - \Delta H_{diln(Cu^{+2})} + \Delta H_{hydn(ligand)}$; $\Delta H_{dilnCu(II)}$ is 12.29 and 12.83 kcal. for 0.4941 and 0.2471 mmole of Cu(II), respectively, in 510 ml. of 50 vol. % dioxane–water.

The changes in free energy were determined from the formation constants and the entropy changes were calculated in the usual manner.

Results

The acid dissociation constants of the various ligands and their formation constants with Cu(II) at 0, 15, and 25° are listed in Table I. Thermodynamic data are given in Table II.

Assuming that ΔH values remain constant over the temperature range studied, Johnston[16] has shown that at pH 4, an error of ±0.01 in the pH reading would result in an error of ±0.025 log unit in the stepwise chelate formation constant or an error of ±0.05 in 2 log K_{av}. This would gave a maximum error in the ΔH° calculated using the temperature coefficient method of ±1.5 kcal., and in ΔS° of ±3.5 e.u.

The ΔH° value obtained calorimetrically for the Cu(II) chelate of 6-methyl-2-pyridylcarbinol is properly defined as the heat of precipitation. This value, however, is in good agreement with that obtained using the temperature coefficient method. All other chelates were soluble under the conditions described, giving a characteristic purple color to the solutions. The absence of the Tyndall phenomenon was also noted.

Discussion

(A) Acid Dissociation Constants.—pK_{NH} of 2-pyridylcarbinol at 25° is 4.16 (Table I). This is slightly lower than the value (4.25) for pyridine in dioxane–water.[17] Normally an increase in basicity would be expected in the 2-carbinol compound because of the electron-releasing effect of the hydroxymethyl group, but the lower value in this compound may be due to strong intramolecular hydrogen bonding between the pyridine nitrogen and the hydroxyl group which would tend to decrease the proton affinity of the nitrogen atom.

In 6-methyl-2-pyridylcarbinol and in 2-(β-hydroxyethyl)pyridine the pK_{NH} has increased at 25° (Table I) to 4.56 and 4.52, respectively. This increase can be attributed to the inductive effect of the added CH_2 groups. 2-(β-Hydroxyethyl)-6-methylpyridine shows a further increase in pK_{NH} value of about 0.6 log unit due to the presence of an additional methyl substituent.

The high pK_{OH} values of these compounds are consistent with the low acidity of alcohols and with the strong intramolecular hydrogen bonding in these compounds.

Both the pK_{NH} and the pK_{OH} values show normal temperature dependence in that they increase with decrease in temperature.

(B) Formation Constants.—The 2 log K_{av} values (Table I) for the 2-pyridylcarbinol and 6-methyl-2-pyridylcarbinol Cu(II) chelates at 25° are 19.15 and 18.35, respectively, indicating almost a tenfold decrease in the stability of the over-all reaction. This effect may be attributed to the steric hindrance caused by the presence of the methyl group in the 6-position. Molecular models show that a methyl group in the 6-position would result in considerable strain in the formation of the 1:2 Cu(II) chelate of 6-methyl-2-pyridylcarbinol. Since the pK_{OH} values of the two compounds are of the same magnitude, a lowering in the ratio of log K_{av}/pK_{NH} would also be indicative of the presence of steric blocking.[2] For 2-pyridylcarbinol this ratio is 2.30, while for the 6-methyl compound it decreases to 2.01. However, the actual numerical difference cannot be used to calculate the magnitude of the steric blocking since log K_{av} values are directly related only to free energy changes.

The difference in the formation constants for the Cu(II) chelates of 2-pyridylcarbinol and of 2-(β-hydroxyethyl)pyridine is 0.61 log unit. This is consistent with the generally observed lower stability of six-membered chelate rings.

(C) Thermodynamic Functions.—Inspection of Table II reveals that ΔH° values estimated using the temperature coefficient method are in good agreement with those obtained by the calorimetric method with the exception of the disagreeing values for 2-pyridylcarbinol. The differences observed (Table II) are difficult to explain. It is known that ΔH values calculated from the temperature coefficient of K_{eq} are

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[16] W. D. Johnston, Ph.D. Thesis, University of Pittsburgh, 1953.

[17] T. J. Lane, *et al.*, results from this laboratory.

sensitive to small errors.[18,19] Charles[20] has reported that large differences are possible as in the case of the determination of the ΔH for the reaction of Mg(II) with EDTA, where the ΔH values disagree even as to the sign. The discussion of the thermodynamics of formation is based on calorimetric data since the accuracy of this method is inherently higher.

The $-\Delta H°$ value for 2-pyridylcarbinol is 23.32 (Table II), while that for 6-methyl-2-pyridylcarbinol is 13.53 kcal./mole. This lower enthalpy value for the 6-methyl compound shows a weakening of the metal–ligand bond caused by the methyl group in the 6-position. A similar, though less pronounced, effect is noticed when comparing 2-(β-hydroxyethyl)pyridine ($-\Delta H° =$ 13.82 kcal./mole) with 2-(β-hydroxyethyl)-6-methylpyridine ($-\Delta H° =$ 12.43 kcal./mole).

The entropy change for the 2-pyridylcarbinol Cu(II) chelate is +9.4 e.u, while that for the 6-methyl compound is +38.1 e.u. (Table II). The much more favorable entropy effect of the latter compound may be attributed to "solvation effects"[21] in which the methyl substituent in the 6-position tends to shield the central metal ion from solvent molecules, thus increasing the total number of particles in the solution. This increased randomness is not sufficient to counteract the steric hindrance, and, as seen from Table I, the 2-pyridylcarbinol chelate is more stable.

The same trend is observed when comparing the 2-(β-hydroxyethyl) chelates. However, a much smaller increase in entropy is noted for 2-(β-hydroxyethyl)-6-methylpyridine (+41.2 e.u.) as compared to 2-(β-hydroxyethyl)pyridine (+38.5 e.u.). This smaller increase seems to indicate that the shielding of the metal atom by the methyl group is less effective in chelates containing six-membered rings.

(D) **Conclusions.**—The results of this study show that the presence of a methyl group in a sterically blocking position in these compounds causes both a bond-weakening effect and a favorable increase in entropy. The stability values indicate that the entropy effect is not large enough to overcome the bond weakening caused by steric hindrance.

[18] F. Basolo and R. K. Murmann, *J. Am. Chem. Soc.*, **76**, 211 (1954).

[19] J. W. Cobble, *J. Chem. Phys.*, **21**, 1451 (1953).

[20] R. G. Charles, *J. Am. Chem. Soc.*, **76**, 5854 (1954).

[21] W. D. Johnston and H. Freiser, *Anal. Chim. Acta*, **11**, 201 (1954).

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Quadridentate Chelate Compounds. IV. Metal Complexes from Butane-2,3-dione Bis(2′-pyridylhydrazone)

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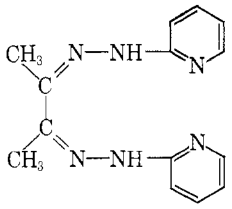
Some planar quadridentate chelate compounds have been prepared from butane-2,3-dione bis(2′-pyridylhydrazone) and transition metal salts favoring square-planar four-coordination [Cu(II), Ni(II), and Pd(II)]. The complex cations of these complex salts could be doubly deprotonated by alkalies and the planar neutral complexes obtained.

Lions and Martin[2] in 1958 reported the interaction of biacetyl and 2-pyridylhydrazine to yield the osazone I and showed that it could function as a planar quadridentate chelating agent. At the same time they reported as an isolated phenomenon the partial deprotonation of the complex cations of a cobalt(III) complex salt containing chelate groups derived from the α-pyridylhydrazone of an aldehyde. Subsequent work[3] has shown the generality of this deprotonation process. It seemed, therefore, to be of value to study some of the complex salts formed from the α-pyridyl osazones of 1,2-diketones and their behavior toward alkalies.



I

α-Dicarbonyl compounds such as glyoxal, biacetyl, and cyclohexane-1,2-dione readily yielded osazones with α-pyridylhydrazine. The present paper reports studies with I.

Using accurate drawings and accepting the usual values for atom sizes and bond angles the arrangement of the molecule of I shows that spatially it would appear to be able to function only imperfectly as a planar quadridentate ligand. Nevertheless, experiment shows that it does so function, giving the salts II with salts of bivalent metals such as copper(II), nickel(II), and palladium(II) (Table I). Treatment of these salts with alkalies leads to deprotonation of their complex cations and formation of the neutral complexes III (Table II). These latter are all soluble in organic solvents and, during preparation, are con-

[1] Petroleum Research Fund Fellow, University of Sydney.

[2] F. Lions and K. V. Martin, *J. Am. Chem. Soc.*, **80**, 3858 (1958).

[3] J. F. Geldard and F. Lions, *ibid.*, **84**, 2262 (1962): *Inorg. Chem.*, **2**, 270 (1963); B. Chiswell and F. Lions, *ibid.*, in press.