# Kinetics of Bromination of Certain Substituted 8-Quinolinols

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▶ A constant current generator and an amperometric indicator system have been used to measure the rates of bromination of 8-quinolinol and its 4-methyl, 5-bromo, 5-chloro, and 5-fluoro derivatives in acid solutions in the presence of bromide ions. An analog computer has been used to obtain the rate constants for the stepwise bromination of 8-quinolinol and 4-methyl-8-quinolinol and for the monobromination of the 5-halo derivatives. There is no evidence of steric hindrance to substitution in the 5-position of 4-methyl-8-quinolinol. In all the 8-quinolinols studied, the bromine molecule was the active brominating agent when bromination occurred in the 5-position, whereas, in every case bromination in the 7-position was accomplished by the tribromide ion as well as by molecular bromine.

THE QUANTITATIVE DIBROMINATION of the chelating agents, 8-quinolinol and 2-methyl-8-quinolinol is the basis for the determination of metal ions which form chelates with these ligands. The metal chelates are precipitated, washed free of excess ligand, dissolved in acid, and the liberated ligand is determined by a bromometric titration. The application of this method to metal chelates formed by other substituted 8-quinolinols has received little attention. Recently, Corsini and Graham (*2*), reported that the dibromination of 4-methyl-8-quinolinol is a relatively slow reaction and takes about twenty minutes to go to completion. The slowness of the reaction was attributed to steric hindrance by the methyl group in 4-position to the monobromination reaction which usually occurs in the 5-position, the position para to the phenolic group. The 4-methyl group might, on the other hand, sterically hinder the introduction of the second bromine atom in the 5-position, if the monobromination reaction occurred in the 7-position. It was decided therefore to resolve this question by carrying out a detailed study of the kinetics of bromination of 4-methyl-8-quinolinol.

In a previous investigation of the kinetics of bromination of 8-quinolinol and 2-methyl-8-quinolinol, the tribromide ion was postulated to be an active brominating species in the second bromination step of 8-quinolinol but not in the first (*4*). In this study, the kinetic data for the bromination of 8-quinolinol have been re-examined with the help of an analog computer, and the kinetics of bromination of a series of 5-substituted 8-quinolinols have been investigated to determine whether the tribromide ion is indeed an active brominating species whenever electrophilic substitution occurs in the 7-position in 8-quinolinol.

## EXPERIMENTAL

**Apparatus.** The apparatus used in this work has been described in detail in a previous paper (*5*). In addition, an E.A.I. Pace Analog Computer Model T.R. 10 and a Moseley Autograph X-Y recorder were used in this study.

**Reagents and Solutions.** Analytical reagent grade perchloric acid and sodium hydroxide, were used in this work without further purification and were also used to prepare sodium perchlorate. Analytical Reagent grade sodium bromide was heated in a muffle furnace for 8–12 hours at about 605° C. before use.

Analytical Reagent grade 8-quinolinol was purified by sublimation under reduced pressure (m.p. 72.5–73.5° C.). 4-Methyl-8-quinolinol was prepared from methyl vinyl ketone and *o*-aminophenol by the Doebner von Miller reaction. The product was recrystallized from ethanol and sublimed under reduced pressure (m.p. 137–8° C.). 5-Bromo-8-quinolinol was prepared by bromination with *N*-bromosuccinimide (*7*), separated from any dibromo compound by selective precipitation and recrystallized from ethanol (m.p. 125° C.). 5-Chloro-8-quinolinol was obtained from Aldrich Chemical Co. and recrystallized from ethanol (m.p. 122° C.). 5-Nitro-8-quinolinol was prepared from 5-nitroso-8-quinolinol, obtained from Aldrich Chemical Co., by the method of Petrow and Sturgeon (*6*) (m.p. 178° C.). 5-Fluoro-8-quinolinol which was obtained from Dr. H. Gershon at the Boyce Thompson Institute, Yonkers, N. Y., was prepared by the Schiemann reaction. The compound was purified by recrystallization from methanol (m.p. 109–10° C.; % C, 65.8 (found), 66.2 (calcd.); % H, 3.60 (found), 3.07 (calcd.); % N, 8.58 (found), 8.59 (calcd.). The NMR spectrum of this compound in trifluoroacetic acid was consistent with that expected for 5-fluoro-8-quinolinol.

All solutions were made as previously described (*5*) and the ionic strength of the solutions used in this study was maintained at a value of 1.35 by the addition of sodium perchlorate.

**Rate Equations.** The reaction scheme can be represented by two parallel consecutive second-order reactions

$$A + B \xrightarrow{k_{1_{obs}}} C \qquad (1)$$

$$C + B \xrightarrow{k_{2_{obs}}} D \qquad (2)$$

where $[A]$ is the total concentration of unreacted 8-quinolinol,

$$[A] = [\mathrm{HOx}] + [\mathrm{H_2Ox^+}] \qquad (3)$$

$[C]$, the total concentration of monobrominated 8-quinolinol,

$$[C] = [\mathrm{HOxBr}] + [\mathrm{H_2OxBr^+}] \qquad (4)$$

and $[D]$ the total concentration of the dibrominated substrate,

$$[D] = [\mathrm{HOxBr_2}] + [\mathrm{H_2OxBr_2^+}] \qquad (5)$$

The following differential equations can be obtained from the reaction scheme:

$$\frac{d(B)}{dt} = R - k_{1_{obs}}[A][B] - k_{2_{obs}}[C][B] \qquad (6)$$

$$-\frac{d[A]}{dt} = k_{1_{obs}}[A][B] \qquad (7)$$

$$-\frac{d[C]}{dt} = k_{2_{obs}}[B][C] - k_{1_{obs}}[A][B] \qquad (8)$$

where $R$ is the rate of generation of bromine, $B$, which is present in solution as molecular bromine and tribromide ions. These equations can be readily solved on an analog computer, and from a knowledge of the concentration, $[B]$, at any time $t$, the rate constants, $k_{1_{obs}}$ and $k_{2_{obs}}$ can be obtained.

**Voltage and Time Scaling on the Analog Computer.** The program used in this study is shown in Figure 1. The difference in the magnitude of $[A]$ and $[B]$ necessitates voltage scaling. The basic variables, $[A]$, $[B]$, $[C]$ and $R$ were scaled. The variable $[B]$ was underscaled since, with the slow reactions, large concentrations of both $[A]$ and $[B]$ are present initially and cause overloading at the amplifier following the multiplier, since amplification by a factor of ten is required. $[B]$ was therefore multiplied by ten before the signal was fed into the multi-

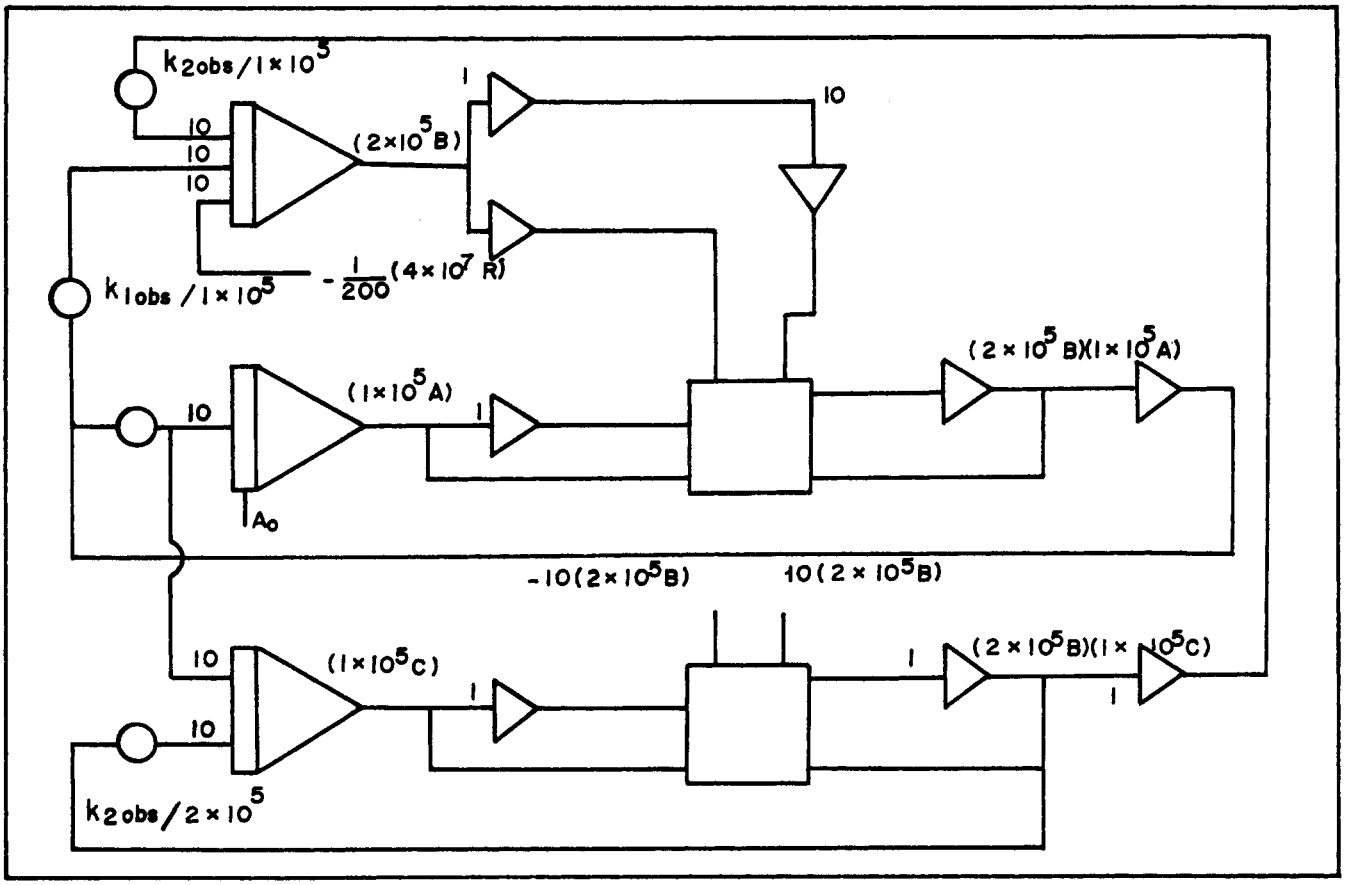


Figure 1. Analog computer program for consecutive parallel second order reactions

pliers to ensure that sufficient voltage was present at the multipliers. The voltage scaling used for the kinetic study of the bromination of 8-quinolinol is shown in Table I. The scaled variable was substituted for the corresponding variable in the differential Equations 6, 7, and 8 to obtain the scaled equations and the concentration–time curves were converted into voltage–time curves which were plotted on an X–Y recorder synchronized with the computer.

In each kinetic experiment, data were recorded for about 400 seconds. Since drift in the computer can occur during such long periods, time scaling was used. A reduction in time by a factor of ten was obtained by increasing the gain across all integrators by a factor of ten.

**Determination of Rate Constants.** The rate constants were obtained from the computer by a method of curve fitting. The concentration–time data were converted into voltage–time data by means of the scale factor for $[B]$ and the resulting curve was plotted on the recorder chart. The initial concentration of $A$ was set on the computer and the attenuators were adjusted until a good fit was obtained with the experimental curve. The attenuation was determined by feeding a reference voltage into the input of the loaded attenuator system and measuring the voltage drop between the attenuator arm and ground by means of a Minneapolis-Honeywell Model 2730 potentiometer. The rate constant was readily calculated from this voltage drop.

Table I. Voltage Scaling for the Analog Computer Kinetic Study of 8-Quinolinol

| Variable | Max. value | Scale factor | Scaled variable |
|---|---|---|---|
| $B$ | $5 \times 10^{-5}M$ | $10V/5 \times 10^{-5}M$ | $[2 \times 10^5 B]$ |
| $A$ | $1 \times 10^{-4}M$ | $10V/1 \times 10^{-4}M$ | $[1 \times 10^5 A]$ |
| $C$ | $1 \times 10^{-4}M$ | $10V/1 \times 10^{-4}M$ | $[1 \times 10^5 C]$ |
| $R$ | $2.5 \times 10^{-7}M$/sec. | $10V/2.5 \times 10^{-7}M$/sec. | $[4 \times 10^7 R]$ |

The rate constants $k_{1_{obs}}$ and $k_{2_{obs}}$ given in Equation 6 can be defined in the following manner:

$$k_{1_{obs}} = \frac{v_1}{([H_2Ox^+] + [HOx])([Br_2] + [Br_3^-])} \quad (9)$$

$$k_{2_{obs}} = \frac{v_2}{([H_2OxBr] + [HOxBr])([Br_2] + [Br_3^-])} \quad (10)$$

where $v_1$ and $v_2$ are the rates of decrease of the total bromine concentration, in the first and second bromination steps, respectively. These rates can also be written in terms of specific rate constants which will be illustrated for the monobromination step.

$$v_1 = k_1[Br_2]([H_2Ox^+] + [HOx]) + k_2[Br_3^-]([H_2Ox^+] + [HOx]) \quad (11)$$

$$v_1 = k_3([Br_2] + [Br_3^-])[HOx] + k_4([Br_2] + [Br_3^-])[H_2Ox^+] \quad (12)$$

Equations 11 and 12, therefore, serve to define the rate constants involved. The same equations can be written for the dibromination step, and the specific rate constants for this reaction are primed—i.e., $k_1'$, $k_2'$, $k_3'$, and $k_4'$.

The above equations are valid for the high acid and bromide ion concentrations used in these experiments, since it can be assumed that only $Br_2$ and $Br_3^-$ are the possible brominating species and that 8-quinolinol is present only in the neutral and protonated forms, the concentration of the anionic form being negligible in these highly acidic solutions.

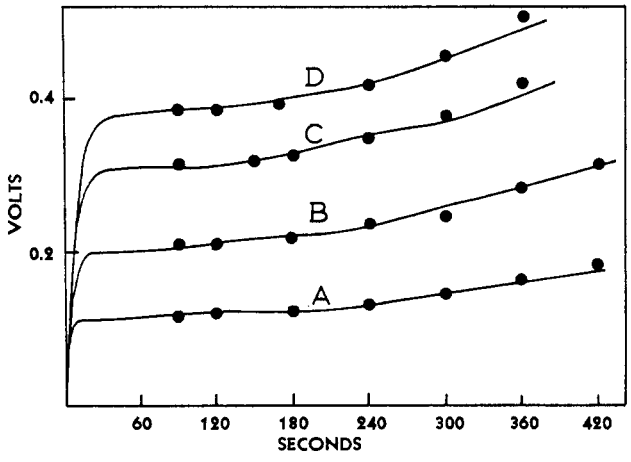


Figure 2. Analog computer curves obtained for the bromination of 8-quinolinol in 0.64M NaBr

●—experimental values

A: 0.05M, B: 0.12M, C: 0.23M, D: 0.35M $HClO_4$

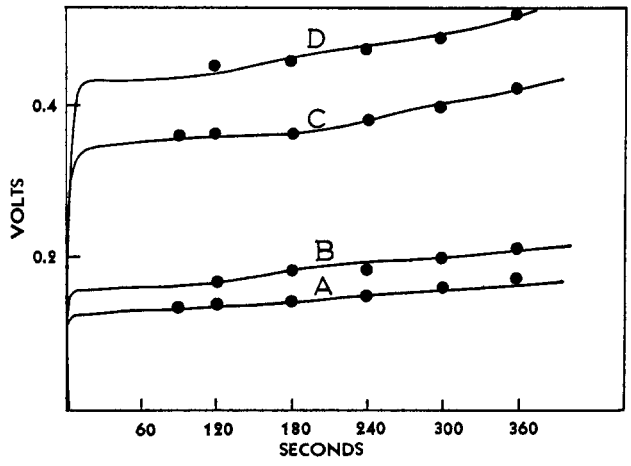


Figure 3. Analog computer curves obtained for the bromination of 4-methyl-8-quinolinol in 0.12M $HClO_4$

●—Experimental values

A: 0.12M, B: 0.24M, C: 0.64M, D: 0.80M NaBr

From data obtained at constant hydrogen ion concentration and varying bromide ion concentration the rate constants $k_1$ and $k_2$ can be obtained from a plot of $k_{1_{obs}}$ $(1 + K\ [Br^-])$ *vs.* $[Br^-]$

$$K = \frac{[Br_3^-]}{[Br_2]\ [Br^-]} = 17 \qquad (13)$$

In a similar manner $k_3$ and $k_4$ are obtained from data at constant $[Br^-]$ and varying $[H^+]$. A plot of $k_{1_{obs}}$ *vs.* $K_{a_1}/[H^+]$, where $K_{a_1}$ is the first acid dissociation constant of the 8-quinolinol and $K_{a_1}/H^+ \ll 1$ will give $k_3$ and $k_4$. The rate constants for the second bromination step can be obtained in exactly the same manner. Therefore the computer values for $k_{1_{obs}}$ and $k_{2_{obs}}$ can be used to determine specific rate constants for the reaction.

All kinetic data for the bromination of the 8-quinolinols, except that for the 5-nitro-8-quinolinol were simulated on the analog computer. The fit of the experimental data with the values obtained for the computer is quite good as shown in Figures 2 and 3 for 8-quinolinol and its 4-methyl derivative. The reproducibility of the computer rate constants is illustrated by the data in Table II for 8-quinolinol. The precision with which $k_{1_{obs}}$ can be determined is $\pm 0.1 \times 10^3$ or better and $k_{2_{obs}}$ can be determined with a precision of about $\pm 0.3 \times 10^3$. Furthermore, a comparison of the $k_{2_{obs}}$ obtained for 8-quinolinol with $k_{2_{obs}}$ for 5-bromo-8-quinolinol in most cases shows good agreement. Thus it appears that the experimental data fit the proposed mechanism and the assumption that electrophilic substitution occurs first in the 5-position of 8-quinolinol and then in the 7-position is justified.

In Tables III and VII two observed constants are listed—i.e. $k_{1_{obs}}$ (computer) and $k_{1_{obs}}$ (calcd.). The calculated values of $k_{1_{obs}}$ were obtained from an analysis of the current-time curves which is valid for simple second order reaction kinetics (3). The rate of bromination of 5-nitro-8-quinolinol was quite rapid and an approximate value of the overall rate constant, $k_{2_{obs}}$, for the monobromination reaction was found to be $2.0 \times 10^{-1} M^{-1}$ second$^{-1}$ in 0.35M $HClO_4$ and $1.4 \times 10^{-4} M^{-1}$ second$^{-1}$ in 0.45M $HClO_4$. The effects of varying bromide ion and hydrogen ion concentrations on the kinetics of bromination of 8-quinolinol is shown in Table III. The kinetic data obtained for the 4-methyl compound are

**Table II. Analog Computer Results for $1.00 \times 10^{-4}$M 8-Quinolinol**

Initial Concentration of $HClO_4$ = 0.23M

| [NaBr] | | Trial 1 | Trial 2 | Average |
|---|---|---|---|---|
| 0.24 | $10^{-3}k_{1_{obs}}$ | 3.48 | 3.50 | 3.49 |
| | $10^{-3}k_{2_{obs}}$ | 3.38 | 3.28 | 3.33 |
| 0.64 | $10^{-3}k_{1_{obs}}$ | 1.65 | 1.85 | 1.75 |
| | $10^{-3}k_{2_{obs}}$ | 1.55 | 1.31 | 1.43 |
| 0.80 | $10^{-3}k_{1_{obs}}$ | 1.34 | 1.40 | 1.37 |
| | $10^{-3}k_{2_{obs}}$ | 1.30 | 1.21 | 1.25 |
| 1.00 | $10^{-3}k_{1_{obs}}$ | 1.16 | 1.15 | 1.16 |
| | $10^{-3}k_{2_{obs}}$ | 0.94 | 0.96 | 0.95 |

Initial Concentration of NaBr = 0.64M

| $[HClO_4]$ | | 1 | 2 | Average |
|---|---|---|---|---|
| 0.05 | $10^{-3}k_{1_{obs}}$ | 4.60 | 4.60 | 4.60 |
| | $10^{-3}k_{2_{obs}}$ | 3.30 | 3.00 | 3.15 |
| 0.12 | $10^{-3}k_{1_{obs}}$ | 2.60 | 2.60 | 2.60 |
| | $10^{-3}k_{2_{obs}}$ | 1.84 | 2.04 | 1.94 |
| 0.23 | $10^{-3}k_{1_{obs}}$ | 1.65 | 1.85 | 1.75 |
| | $10^{-3}k_{2_{obs}}$ | 1.55 | 1.31 | 1.43 |
| 0.35 | $10^{-3}k_{1_{obs}}$ | 1.34 | 1.35 | 1.35 |
| | $10^{-3}k_{2_{obs}}$ | 1.30 | 1.31 | 1.31 |

**Table III. The Effect of Bromide and Hydrogen Ions on the Bromination of $1.00 \times 10^{-4}$M 8-Quinolinol**

| $[HClO_4]$ | [NaBr] | $10^{-3}k_{2_{obs}}$ Calcd. | $10^{-3}k_{2_{obs}}$ Computer | $10^{-3}k_{2_{obs}}(1 + K \times [Br^-])$ | $10^5 K_{a_1}/[H^+]$ |
|---|---|---|---|---|---|
| 0.23 | 0.24 | 3.91 | 3.49 | 17.7 | ... |
| 0.23 | 0.64 | 1.97 | 1.75 | 20.8 | ... |
| 0.23 | 0.80 | 1.60 | 1.37 | 20.0 | ... |
| 0.23 | 1.00 | 1.97 | 1.16 | 20.9 | ... |
| 0.05 | 0.64 | 5.48 | 4.60 | ... | 13.88 |
| 0.12 | 0.64 | 3.02 | 2.60 | ... | 5.78 |
| 0.23 | 0.64 | 1.97 | 1.75 | ... | 3.02 |
| 0.35 | 0.64 | 1.74 | 1.35 | ... | 1.98 |

$K_{a1} = 6.94 \times 10^{-6}$

Table IV. The Effect of Bromide Ion Concentration on the Bromination of 1.36 × 10⁻⁴M 4-Methyl-8-Quinolinol

| [HClO₄] | [NaBr] | $10^{-3}k_{1obs}$ Calcd. | $10^{-3}k_{1obs}$ Computer | $10^{-4}k_{1obs}$ $(1 + K[Br^-])$ |
|---|---|---|---|---|
| 0.12 | 0.12 | 7.88 | 7.30 | 2.22 |
| 0.12 | 0.24 | 6.59 | 5.89 | 2.99 |
| 0.12 | 0.64 | 3.00 | 2.74 | 3.26 |
| 0.12 | 0.80 | 2.54 | 2.10 | 3.07 |
| 0.12 | 1.00 | 2.03 | 1.62 | 2.92 |
| 0.23 | 0.12 | 7.00 | 6.36 | 1.93 |
| 0.23 | 0.24 | 5.00 | 4.11 | 2.09 |
| 0.23 | 0.64 | 2.05 | 1.65 | 1.96 |
| 0.23 | 0.80 | 1.61 | 1.32 | 1.93 |
| 0.23 | 1.00 | 1.24 | 1.02 | 1.84 |
| 0.35 | 0.12 | 6.33 | 5.17 | 1.57 |
| 0.35 | 0.24 | 4.10 | 3.41 | 1.73 |
| 0.35 | 0.64 | 1.61 | 1.35 | 1.60 |
| 0.35 | 0.80 | 1.23 | 1.01 | 1.48 |
| 0.35 | 1.00 | 1.00 | 0.78 | 1.40 |

Table V. The Effect of Hydrogen Ion Concentration on the Bromination of 1.36 × 10⁻⁴M 4-Methyl-8-Quinolinol in 0.64M NaBr

| [HClO₄] | $10^{-3}k_{1obs}$ Calcd. | $10^{-3}k_{1obs}$ Computer | $10^6K_{a1}/[H^+]$ | $10^{-4}[H^+]/K_{a1}$ |
|---|---|---|---|---|
| 0.05 | 4.77 | 4.05 | 54.00 | 1.85 |
| 0.07 | 4.02 | 3.57 | 38.57 | 2.59 |
| 0.095 | 3.25 | 2.92 | 28.46 | 3.52 |
| 0.12 | 3.00 | 2.69 | 22.50 | 4.44 |
| 0.23 | 2.05 | 1.65 | 11.74 | 8.52 |
| 0.35 | 1.61 | 1.35 | 7.71 | 12.96 |
| 0.47 | 1.36 | 1.12 | 5.74 | 17.40 |

$K'_{a1} = 2.7 \times 10^{-6}$

Table VI. The Effect of Bromide Ion Concentration on the Second Bromination Step of 1.36 × 10⁻⁴M 4-Methyl-8-Quinolinol

| [HClO₄] | [NaBr] | $10^{-3}k_{2obs}$ | $10^{-3}k_{2obs}$ $(1 + K[Br^-])$ |
|---|---|---|---|
| 0.12 | 0.12 | 4.28 | 13.0 |
| 0.12 | 0.24 | 3.09 | 15.7 |
| 0.12 | 0.64 | 2.29 | 27.2 |
| 0.12 | 0.80 | 2.04 | 29.8 |
| 0.12 | 1.00 | 1.90 | 34.0 |
| 0.23 | 0.12 | 3.93 | 11.9 |
| 0.23 | 0.24 | 3.41 | 17.3 |
| 0.23 | 0.64 | 1.60 | 19.0 |
| 0.23 | 0.80 | 1.37 | 20.0 |
| 0.23 | 1.00 | 1.18 | 21.2 |
| 0.35 | 0.12 | 3.95 | 12.0 |
| 0.35 | 0.24 | 2.86 | 14.5 |
| 0.35 | 0.64 | 1.28 | 15.2 |
| 0.35 | 0.80 | 1.12 | 16.3 |
| 0.35 | 1.00 | 0.84 | 15.1 |

Table VII. The Effect of Hydrogen Ion Concentration on the Second Bromination of 1.36 × 10⁻⁴M 4-Methyl-8-Quinolinol in 0.64M NaBr

| [HClO₄] | $10^{-3}k_{2obs}$ | $10^{-4}K'_{a_1}/[H^+]$ | $10^{-2}[H^+]/K'_{a_1}$ |
|---|---|---|---|
| 0.05 | 4.26 | 23.2 | 4.31 |
| 0.07 | 3.35 | 16.57 | 6.02 |
| 0.095 | 2.99 | 12.21 | 8.19 |
| 0.12 | 2.29 | 9.67 | 10.34 |
| 0.23 | 1.59 | 5.04 | 19.83 |
| 0.35 | 1.28 | 3.31 | 30.17 |
| 0.47 | 1.04 | 2.47 | 40.52 |

$K'_{a1} = 2.7 \times 10^{-6}$

summarized in Tables IV to VII. The specific rate constants obtained from these data are compared in Table VIII.

## DISCUSSION

An analysis of the data for 8-quinolinol shows that the plot of $k_{1obs}$ $(1 + K[Br^-])$ *vs.* $[Br^-]$ is a straight line of zero slope. Furthermore, it is seen that the rate constant for the bromination of the neutral species is about $10^4$ times greater than that of the protonated species. This is in agreement with a previous study of some 8-quinolinols (*4*).

The results obtained for the 4-methyl compound are quite unexpected in view of the work reported by Corsini and Graham (*2*). Little difference was found between the behavior of 8-quinolinol and its 4-methyl derivative. The values of $k_{1obs}$ and $k_{2obs}$ for 4-methyl-8-quinolinol are approximately equal to one another and to those obtained for 8-quinolinol. The data for the monobromination of 4-methyl-8-quinolinol show that the tribromide ion is not an active brominating species and here again the neutral species is much more reactive than the protonated species.

The neutral species also brominates with a rate constant which is much larger than that for the protonated species in the bromination of the halo substituted compounds. The rate constant for the neutral species of 8-quinolinol, furthermore, was about 10 times that for the 5-bromo derivative. These rate constants, however, refer to bromination at different sites (the 5 and the 7 position) and the difference may not, therefore, be entirely due to halogen deactivation. Furthermore, the rate constants for the neutral halo substituted 8-quinolinols follow the order bromo~chloro>fluoro.

An interesting result which has emerged from this work is that the tribromide ion is not an active brominating species in the first bromination step of 8-quinolinol or the 4-methyl compound. In the second bromination step of the two compounds, however, as well as in the bromination of the 5-chloro and 5-fluoro compounds, the tribromide ion is an active brominating species. In all cases a positive slope is obtained when values of $k_{2obs}$ $(1 + K[Br^-])$ are plotted against $[Br^-]$. These slopes increase when the hydrogen ion concentration is decreased. In all cases, however, the rate constant for

Table VIII. Summary of Rate Constants

| | $10^{-4} \times k_1$ or $10^{-4} \times k_1'$ | | | $10^{-2} \times k_2$ or $10^{-2} \times k_2'$ | | | $10^{-6} \times k_3$ or $10^{-6} \times k_3'$ | $10^{-2} \times k_4$ or $10^{-2} \times k_4'$ |
|---|---|---|---|---|---|---|---|---|
| Molarity of $HClO_4$ | 0.12 | 0.23 | 0.35 | 0.12 | 0.12 | 0.35 | | |
| 8-Quinolinol | ... | 2.0 | ... | ... | 0 | ... | 26 | 8 |
| 5-Bromo-8-quinolinol | 2.4 | 1.6 | ... | 7 | 2.4 | ... | 2.0 | 1 |
| 4-Methyl-8-quinolinol | 3.1 | 1.6 | ... | ... | ... | ... | 75 | 7.5 |
| 4-Methyl-5-bromo-8-quinolinol | 1 | 1.6 | 1.3 | 14 | 3 | 1.5 | 1.5 | 8 |
| 5-Chloro-8-quinolinol | 1.6 | ... | ... | 9 | ... | ... | 1.6 | 2.5 |
| 5-Fluoro-8-quinolinol | ... | 0.4 | ... | ... | 0.7 | ... | 0.65 | 1.7 |

tribromide bromination is about 1–2% that of molecular bromine. Therefore tribromide ion is a less reactive brominating agent than molecular bromine as was found previously for aromatic bromination (*1*). The above results for tribromide ion activity in substituted 8-quinolinols agree with a previous observation (*4*), that in 8-quinolinols substitution in the seven position occurs *via* the attack of the tribromide ion as well as by molecular bromine, whereas substitution in the 5-position takes place only via attack of a bromine molecule.

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RECEIVED for review December 9, 1965. Accepted March 16, 1966. Work supported by the National Institutes of Health.


# Intermolecular Energy Transfer as a Means of Chemical Analysis

## Sensitization of Rare Earth Emission in Dilute Solution by Aromatic Carbonyl Compounds


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▶ **The fluorescence emission of terbium, europium, samarium, and dysprosium ions is selectively sensitized by various aromatic carbonyl compounds. The system is excited by monochromatic light at the wavelength of maximum absorption for the phosphorescence transition of the carbonyl compound, and emission is measured at the wavelength corresponding to the rare earth ion emission line. The influence of donor-acceptor concentration on the emission intensity of the rare earth ion is studied, and limits of detection for the rare earths are given. An empirical equation is developed to facilitate prediction of sensitization by a specific aromatic carbonyl compound for a specific rare earth. The analytical possibilities of the new phenomenon are discussed with regard to sensitivity, selectivity, and speed of analysis and other analytically important considerations.**


AN INVESTIGATION of the emission of several rare earth ions in chelates by the method of intramolecular energy transfer resulted in the discovery of a new phenomenon. This phenomenon, the intermolecular energy transfer from excited organic compounds to rare earth ions in solution (*7, 9, 10 13*), seems to possess great analytical possibilities for several reasons: The method should be nearly as selective as any atomic emission procedure because the line emission from an ion in solution is being measured, and even more selectivity should arise because various organic compounds transfer their energy with widely different efficiencies to different rare earth ions.

Analytical considerations such as speed, accuracy, precision, and convenience have not been previously studied for the phenomenon and were included in this investigation. Commercially available instrumentation is used for these studies.

### THEORY

The phenomenon of intramolecular energy transfer in rare earth chelates is well known, but it has received little attention from an analytical standpoint, probably because of the stoichiometric dependence of the sensitized emission. The process of intramolecular energy transfer has been described in the past few years in detail by Weissman (*21*) and Crosby and coworkers (*4–6, 8*). The ligand molecules are raised to the first excited singlet state by absorption of a photon which approximately corresponds in energy to the absorption energy of the uncomplexed ligand; the spectral shift is, of course, due to the presence of the ligand in the chelate rather than simply the uncomplexed ligand. After a radiationless crossover to the triplet state of the ligand, energy is transferred to the metal ion in the chelate, raising the metal ion to an excited (luminescent) level. As the excited ion undergoes a radiational deactivation to the ground state, the sensitized emission of the metal ion is observed. This type of energy transfer has been applied to a number of cases of analytical interest. Two articles (*2, 18*) have reviewed the state of the method through 1962; recently a new method utilizing intramolecular energy transfer has been developed for the determination of Sm, Tb, Dy, and Eu (*1*).

Recently, however, sensitized emission from nonchelated rare earth ions in solution has been observed. Matovick and Suzuki (*13*) observed that $Eu(NO_3)_3$ and $Tb(NO_3)_3$ fluoresce strongly in solutions of acetophenone, propiophenone, and benzophenone when irradiated with long wavelength ultraviolet light (3000 to 4000 A.). They found that water strongly quenched the emission of the rare earth ions. They concluded that the mechanism of excitation for the rare earth ion was through a weakly bonded ketone complex. They suggested that the process was probably endothermic, which would account for the observed rise in the quantum efficiency with increased temperature.

El-Sayed and Bhaumik (*7*) observed that benzophenone efficiently transferred its energy to an europium chelate (europium trishexafluoroacetylacetonate) at room temperatures. They suggested initial intermolecular transfer of triplet state energy from the benzophenone to the ligand and subsequent intramolecular transfer of energy to the europium ion as the mechanism of the process. A tenfold increase in europium ion emission upon addition of the benzophenone donor was reported by these authors. Because of temperature variations of the intensity of rare earth emission, a diffusion-controlled process was shown to exist rather than the weak