which is equivalent to eq 2 with $\rho = \alpha$ and $\rho\delta = \beta$. Then $\rho$ or $\alpha$ may be used as a measure of the magnitude of the electrical effect.

Sets 1B, 3, 5, and 9 permit a test of eq 9. The results obtained are $p = 0.773$, $\rho_A{}^\circ = 1.11$, $r = 0.973$, $s = 0.0906$, $s_p = 0.130$, and $t = 5.953$. The results show that this relationship apparently is obeyed. Unfortunately the limited number of values available does not provide a conclusive test. The data available do not permit any discussion of the variation of $\rho$ with temperature or solvent.

It is of interest to compare the magnitude of electrical effects on charge-transfer complex formation with that of reactions of substituted benzenes. For electrophilic aromatic substitution[7] the value of $\rho$ ranges from $-2.4$ to $-12.1$, while for hydrogen–deuterium exchange in the *para* position of substituted benzenes in liquid ammonia a $\rho$ value of 5.6 is obtained.[11] The magnitude of $\rho$ for charge-transfer complex formation in substituted benzenes is in general much smaller than the $\rho$ values quoted above.

**Steric Effects.**—The peculiar effect of the isopropyl group in sets 11 and 13 is probably due to a steric effect. In the 1 position of naphthalene the isopropyl group is forced into a position in which its terminal methyl groups are above and below the plane of the naphthalene ring. This should prevent a close approach of donor and acceptor, and therefore decrease the value of the equilibrium constant. In the 2 position, the isopropyl group can adopt a conformation which places both methyl groups on one side of the plane of the ring, thus there is no steric effect for this group in the 2 position. A steric effect is observed for the tertiary butyl group in the 2 position (set 14), because any conformation of this group results in at least one terminal methyl group on each side of the ring. These conclusions are in accord with a number of observations reported in the literature of steric effects on complex formation.[3]

[11] From a correlation of data reported by A. I. Shatenshtein, *Tetrahedron*, **18**, 95 (1962).

---

# Application of the Hammett Equation to Substituent Effects on π Donors in Charge-Transfer Complex Formation. II. Multiply Substituted Donors

MARVIN CHARTON

*Department of Chemistry, School of Enginneering and Science, Pratt Institute, Brooklyn, New York 11205*

Charge-transfer complex formation constants for 23 sets of $C_6H_{6-n}Me_n$ donors with halogen, $SO_2$, silver(I) ion, and $\pi$ acceptors, one set of $C_6H_{6-n}Et_n$ donors with ICl as acceptor, and two sets of $C_6H_{6-n}F_n$ with $I_2$ as acceptor were successfully correlated with the Andrews–Keefer equation, $\log K_n = bn + d$. This equation may be derived from the extended Hammett equation for multiple substitution, $Q_{X_1 \ldots X_n} = \alpha\Sigma\sigma_{I,X} + \beta\Sigma\sigma_{R,X} + Q_H$ *if all positions in the benzene ring are equivalent with respect to charge-transfer complex formation.* The validity of the derivation is substantiated by the agreement between values of $b$ calculated from appropriate $\alpha$ and $\beta$ values obtained in previous work and the values of $b$ obtained from the correlations. The importance of steric effects in polysubstituted benzenes is discussed. It is proposed that a statistical factor of 2 be applied to those polysubstituted benzene donors in which only one side of the benzene ring is capable of charge-transfer complex formation.

In the first paper of this series[1] we have examined substituent effects on charge-transfer complex formation in monosubstituted $\pi$ donors. We now extend our studies to the problem of multiply substituted benzene $\pi$ donors. Andrews and Keefer have proposed the equation

$$\log K_n = bn + d \tag{1}$$

for the correlation of complex formation constants of $C_6H_{6-n}R_n$ (R = alkyl). In the absence of steric effects a linear relationship is obtained.

We will approach this problem by means of the Hammett equation[2]

$$Q_X = \rho\sigma_X + Q_H \tag{2}$$

which in its extended form is

$$Q_X = \alpha\sigma_I + \beta\sigma_R + Q_H \tag{3}$$

To a reasonable approximation, the effect of several substituents may be expressed by the relationship

$$Q_{X_1 \ldots X_n} = \rho\Sigma\sigma_{X_i} + Q_H \tag{4}$$

where

$$\Sigma\sigma_{X_i} = \sigma_{X_1} + \sigma_{X_2} + \ldots\sigma_{X_n} \tag{5}$$

Applied to the extended form of the Hammett equation (eq 3) this relationship takes the form

$$Q_{X_1 \ldots X_n} = \alpha\Sigma\sigma_{I,X_i} + \beta\Sigma\sigma_{R,X_i} + Q_H \tag{6}$$

where

$$\Sigma\sigma_I = \sigma_{I,X_1} + \sigma_{I,X_2} + \ldots\sigma_{I,X_n} \qquad (7)$$

$$\Sigma\sigma_R = \sigma_{R,X_1} + \sigma_{R,X_2} + \ldots\sigma_{R,X_n} \qquad (7)$$

If the substituents present are identical and are situated in equivalent positions

$$\sigma_{I,X_1} = \sigma_{I,X_2} = \sigma_{I,X_n};\ \sigma_{R,X_1} = \sigma_{R,X_2} = \sigma_{R,X_n} \tag{8}$$

and

$$\Sigma\sigma_{I,X_i} = n\sigma_{I,X};\ \Sigma\sigma_{R,X} = n\sigma_{R,X} \tag{9}$$

giving

$$Q_{X_i \ldots X_n} = \alpha n\sigma_{I,X} + \beta n\sigma_{R,X} + Q_H \tag{10}$$

---

[1] M. Charton, Abstracts, 146th National Meeting of the American Chemical Society, Denver, Colo., Jan 1964, p 31–D; *J. Org. Chem.*, **31**, 2991 (1966).

[2] H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953); R. W. Taft, Jr., "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, p 565; V. Palm, *Russ. Chem. Rev.*, **31**, 471 (1961); P. R. Wells, *Chem. Rev.*, **63**, 171 (1963); C. D. Ritchie and W. F. Sager, Jr., *Progr. Phys. Org. Chem.*, **2**, 323 (1963).

As the only variable on the right side of 10 is $n$

$$Q_{X_1\ldots X_n} = (\alpha\sigma_{I,X} + \beta\sigma_{R,X})n + Q_H \quad (11)$$

which is equivalent to eq 1 with

$$b = \alpha\sigma_{I,X} + \beta\sigma_{R,X} \quad d = Q_H \quad (12)$$

We have examined the correlation of data taken from the literature with eq 1. The data used are set forth in Table I. The results of the correlations by least-mean squares are given in Table II.

## Results

For those sets with halogen or sulfur dioxide as acceptors and methylbenzenes as donors, excellent correlations were generally obtained (sets 1–8). Of the sets in which nitrobenzenes and methylbenzenes are acceptors and donors, respectively (sets 9–17), excellent results were obtained with sets 9–12 and 15 as is shown by the confidence level (cl = 99.9). Results for sets 12 and 15 were improved slightly by omission of the values for $n = 1$ and $n = 0$, respectively. Sets 14 and 17 gave very good correlation (cl = 99.0). Omission of the value for $n = 1$ from set 14 somewhat improved the results. Set 16 gave good correlation which was not significantly improved by omission of the value for $n = 1$. Set 13 gave a poor correlation, however the omission of the value for $n = 1$ gave excellent results.

Excellent correlations were obtained with chloranil (set 18), 7,7,8,8-tetracyanoquinodimethane (set 19), and tetracyanoethylene (set 21) as acceptors and methylbenzenes as donors. With pyromellitic anhydride as the acceptor and methylbenzenes as donors very good results were obtained.

The sets 22 and 23 in which the acceptor is silver(I) ion and the donors are methylbenzenes gave no significant correlation. We believe this is due to the geometry of the silver(I) complexes which makes them particularly susceptible to steric effects.

In sets 24 and 25 in which iodine is the acceptor and fluorobenzenes are the donors, the results are very good. With iodine monochloride as the acceptor and ethylbenzenes as donors (set 26) the results are excellent as judged by the confidence level. The results are not quite so good as those obtained for sets 5 and 6 (the data are from the same source). There is a possibility of steric hindrance in the 1,2,4-triethyl-1,2,3,5-tetraethyl- and 1,2,4,5-tetraethylbenzenes which may account for this observation. We shall discuss this point in more detail below.

## Discussion

**The Equivalence of Positions on the Benzene Ring in Charge-Transfer Complex Formation.**—Our results show that certainly for the methyl group and probably for fluorine and ethyl as well, eq 1 is obeyed. Then, for these substituents at least, all positions on the benzene ring are equivalent in charge-transfer complex formation. It seems likely that in the absence of steric effects this conclusion will be generally applicable to alkyl and probably to halogen substituents. The lack of data makes it impossible to determine whether this equivalence is generally true. It is certainly not true for the 1 and 2 positions in naphthalene, as we have shown previously that the composition of the electrical effect of a substituent in the 1 position is significantly different from that of the same substituent in the 2 position.

In polysubstituted benzenes, it seems likely that eq 6 is applicable. Unfortunately, no data are available which would permit a test of eq 6 for these compounds.

**The Validity of the Derivation of Eq 1.**—We have shown that an equation analogous to eq 1 may be derived from the extended Hammett equation. To provide further evidence for the validity of the derivation we have calculated $b$ from eq 12 using values of $\alpha$ and $\beta$ obtained in the first paper of this series. The results are set forth in Table III, as are also the values of $Q_H$ (again from the first paper of this series). To provide a further comparison of $b$ values for set 25 we have correlated the formation constants of Tamres[3] for iodine-substituted benzenes in heptane at 21° with the equation

$$Q_X = \alpha\Sigma\sigma_I + \beta\Sigma\sigma_R + Q_H \quad (13)$$

The data used are given in Table IV. The source of the $\sigma$ constants used is given in the first paper of this series. The results of this correlation are $\alpha = -2.27$, $\beta = -1.47$, $Q_H = 0.0413$, $R = 0.991$, $s_{est} = 0.0673$, $s_\alpha = 0.277$, $s_\beta = 0.325$, $F = 108.7$, $r = 0.962$. Tamres had reported that these formation constants are correlated by the Taft $\sigma^*$ constants, which are proportional to the $\sigma_I$ constants. We find a significant resonance effect however, as is shown by the value of $\beta$.

The agreement between $d_1$ and $d_{12}$ is generally very good. The $b_{12}$ values for the sets of methylbenzene donors are all less than the $b_1$ values, the average value of $b_{12}/b_1$ being about 0.8. This may be due to errors in the values of $\sigma_I$ and $\sigma_R$ for the methyl group. Equation 12 may be solved for $\sigma_I$ and $\sigma_R$ using the known values of $\alpha$, $\beta$, and $b_1$. On so doing, we obtain $\sigma_I = -0.04$, $\sigma_R = -0.18$. The value of $\sigma_I$ obtained is in good agreement with the reported value of $-0.05$.[4] The value of $\sigma_R$ found here is just barely significantly larger than the value of $-0.12$ previously used.[4]

**Steric Effects on the Equivalence of Positions in Benzene.**—We have remarked above that in certain of the ethylbenzenes there may be steric hindrance to complex formation. Examination of models shows that in the tetraethylbenzenes one side of the benzene ring can be unhindered, whereas the other side must be hindered. Some interference on one side of the ring in 1,2,4-triethylbenzene also seems likely. Elimination of these compounds (set 26A) gives a better correlation coefficient but a lower confidence level due to the smaller size of the set. Let us consider the following postulate, that, due to steric hindrance, only one side of the benzene ring in the tetraethylbenzenes is capable of complex formation. Then, since the other members of the set can enter into complex formation with equal probability on either side of the benzene ring, we must introduce a statistical factor of 2 in order to include the tetraethylbenzenes in the set. As the steric hindrance on one side of 1,2,4-triethylbenzene is not severe enough to justify the above postulate, we cannot determine an appropriate statistical factor for this compound. We, therefore, exclude it from the set to obtain, with no statistical factor, set 26B, and,

---

[3] M. Tamres, *J. Phys. Chem.*, **68**, 2621 (1964).

[4] Sources of the $\sigma$ constants used are given in ref 1.

## TABLE I

### CHARGE-TRANSFER COMPLEX FORMATION CONSTANTS USED IN CORRELATIONS[a]

1. Bromine–methylbenzenes in $CCl_4$ at 25°[b]

| $n$ | 0 | 1 | 2 (1,2) | 2 (1,3) | 2 (1,4) |
|---|---|---|---|---|---|
| $K_N$ | 1.04 | 1.44 | 2.29 | 2.16 | 2.26 |

2. Iodine–methylbenzenes in $CCl_4$ at 25°[c]

| $n$ | 0 | 1 | 2 (1,2) | 2 (1,3) | 2 (1,4) | 3 (1,3,5) | 4 | 5 | 6 |
|---|---|---|---|---|---|---|---|---|---|
| $K_C$ | 0.15 | 0.16 | 0.27 | 0.31 | 0.31 | 0.82 | 0.63 | 0.88 | 1.35 |

3. Iodine–methylbenzenes in $CCl_4$ at room temperature[d]

| $n$ | 0 | 3 (1,3,5) | 4 (1,2,3,5) | 5 | 6 |
|---|---|---|---|---|---|
| $K_N$ | 1.60 | 5.96 | 6.87 | 9.72 | 15.2 |

4. Iodine monochloride–methylbenzene in $CCl_4$ at 25°[e]

| $n$ | 0 | 1 | 2 (1,2) | 2 (1,3) | 2 (1,4) |
|---|---|---|---|---|---|
| $K_N$ | 4.76 | 7.97 | 15.4 | 16.0 | 13.4 |

5. Iodine monochloride–methylbenzene in $CCl_4$ at 25°[c]

| $n$ | 0 | 1 | 2 (1,2) | 2 (1,3) | 2 (1,4) | 3 (1,3,5) | 4 (1,2,4,5) | 5 | 6 |
|---|---|---|---|---|---|---|---|---|---|
| $K_C$ | 0.54 | 0.87 | 1.24 | 1.39 | 1.51 | 4.59 | 4.25 | 6.43 | 22.7 |

6. Iodine monochloride–methylbenzene in $CCl_4$ at 25°[f]

| $n$ | 2 (1,2) | 3 (1,2,4) | 3 (1,3,5) | 4 (1,2,3,4) | 4 (1,2,3,5) | 6 |
|---|---|---|---|---|---|---|
| $K_C$ | 1.85 | 2.82 | 3.70 | 3.99 | 5.60 | 13.2 |

7. Iodine monobromide–methylbenzene in $CCl_4$ at 24°[g]

| $n$ | 0 | 1 | 2 (1,2) | 2 (1,3) | 2 (1,4) | 3 (1,3,5) | 6 |
|---|---|---|---|---|---|---|---|
| $K_C$ | 0.44 | 0.51 | 0.78 | 0.78 | 0.67 | 1.47 | 4.3 |

8. Sulfur dioxide–methylbenzene in $CCl_4$ at 25°[h]

| $n$ | 0 | 1 | 2 (1,3) | 2 (1,4) | 2 (1,2) | 3 |
|---|---|---|---|---|---|---|
| $K_N$ | 0.47 | 0.79 | 1.49 | 1.34 | 1.65 | 2.11 |

9. 1,3,5-Trinitrobenzene–methylbenzene in $CCl_4$ at 20°[i]

| $n$ | 0 | 1 | 2 (1,3) | 4 (1,2,4,5) | 6 |
|---|---|---|---|---|---|
| $K_C^{-1}$ | 4.30 | 2.42 | 1.15 | 0.426 | 0.141 |

10. 1,3,5-Trinitrobenzene–methylbenzene in $CCl_4$ at 33.5°[j]

| $n$ | 0 | 1 | 2 (1,2) | 3 (1,3,5) | 4 (1,2,4,5) | 5 | 6 |
|---|---|---|---|---|---|---|---|
| $K_C$ | 0.315 | 0.423 | 0.577 | 0.797 | 1.320 | 1.935 | 3.208 |

11. 1,3,5-Trinitrobenzene–methylbenzene in $CCl_4$ at 20°[k]

| $n$ | 1 | 2 (1,3) | 3 (1,3,5) | 4 (1,2,4,5) | 5 | 6 |
|---|---|---|---|---|---|---|
| $K_C$ | 0.33 | 0.41 | 0.70 | 1.91 | 3.25 | 4.92 |

12. 1,3,5-Trinitrobenzene–methylbenzene in $CCl_4$ at 45°[k]

| $n$ | 1 | 2 (1,3) | 3 (1,3,5) | 4 (1,2,4,5) | 5 | 6 |
|---|---|---|---|---|---|---|
| $K_C$ | 0.25 | 0.26 | 0.55 | 1.21 | 1.93 | 3.07 |

13. 2,4,6-Trinitrotoluene–methylbenzene in $CCl_4$ at 20°[k]

| $n$ | 1 | 2 (1,3) | 3 (1,3,5) | 4 (1,2,4,5) | 5 | 6 |
|---|---|---|---|---|---|---|
| $K_C$ | 0.75 | 0.45 | 0.52 | 0.68 | 1.19 | 1.61 |

14. 2,4,6-Trinitrotoluene–methylbenzene in $CCl_4$ at 45°[k]

| $n$ | 1 | 2 (1,3) | 3 (1,3,5) | 4 (1,2,4,5) | 5 | 6 |
|---|---|---|---|---|---|---|
| $K_C$ | 0.26 | 0.17 | 0.38 | 0.58 | 0.94 | 1.17 |

15. 1,4-Dinitrobenzene–methylbenzene in $CCl_4$ at 33.5°[j]

| $n$ | 0 | 1 | 2 (1,2) | 3 (1,3,5) | 4 (1,2,4,5) | 5 | 6 |
|---|---|---|---|---|---|---|---|
| $K_C$ | 0.168 | 0.170 | 0.219 | 0.259 | 0.390 | 0.470 | 0.636 |

16. 1,4-Dinitrobenzene–methylbenzene in $CCl_4$ at 20°[k]

| $n$ | 1 | 2 (1,3) | 4 (1,2,4,5) | 5 | 6 |
|---|---|---|---|---|---|
| $K_C$ | 0.21 | 0.16 | 0.41 | 0.79 | 0.82 |

17. 1,4-Dinitrobenzene–methylbenzene in $CCl_4$ at 45°[k]

| $n$ | 1 | 2 (1,3) | 4 (1,2,4,5) | 5 | 6 |
|---|---|---|---|---|---|
| $K_C$ | 0.06 | 0.09 | 0.64 | 0.76 | 0.99 |

18. Chloranil–methylbenzene in cyclohexane at 18–20°[l]

| $n$ | 0 | 1 | 2 (1,3) | 3 (1,3,5) | 4 (1,2,4,5) | 5 | 6 |
|---|---|---|---|---|---|---|---|
| $K_C$ | 0.56 | 1.7 | 2.9 | 5.9 | 10.4 | 16.5 | 28.9 |

19. 7,7,8,8-Tetracyanoquinodimethane–methylbenzene in dioxane at 37°[m]

| $n$ | 0 | 1 | 2 (1,2) | 2 (1,3) | 2 (1,4) | 3 (1,3,5) | 4 (1,2,4,5) | 5 | 6 |
|---|---|---|---|---|---|---|---|---|---|
| $K_K$ | 0.061 | 0.085 | 0.12 | 0.12 | 0.12 | 0.16 | 0.33 | 0.55 | 1.15 |

20. Pyromellitic anhydride–methylbenzene in $CCl_4$ at 26°[n]

| $n$ | 0 | 1 | 2 (1,2) | 2 (1,3) | 2 (1,4) |
|---|---|---|---|---|---|
| $K_N$ | 3.05 | 5.03 | 10.3 | 7.60 | 8.25 |

21. Tetracyanoethylene–methylbenzene in $CH_2Cl_2$ at 22°[o]

| $n$ | 0 | 1 | 2 (1,2) | 2 (1,3) | 2 (1,4) | 3 (1,3,5) | 4 (1,2,4,5) | 5 | 6 |
|---|---|---|---|---|---|---|---|---|---|
| $K_N$ | 2.00 | 3.70 | 6.97 | 6.00 | 7.64 | 17.3 | 54.2 | 123 | 263 |

22. Silver ion–methylbenzene in water at 25°[p,q]

| $n$ | 0 | 1 | 2 (1,2) | 2 (1,3) | 2 (1,4) | 3 (1,3,5) |
|---|---|---|---|---|---|---|
| $K_C$ | 2.41 | 2.95 | 2.89 | 3.03 | 2.63 | 1.80 |

TABLE I (*Continued*)

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 23. | Silver ion–methylbenzene in equimolar $H_2O$–MeOH at 25°, $\mu = 0.5$[r] | | | | | | |
| $n$ | 0 | 1 | 2 (1,2) | 2 (1,3) | 2 (1,4) | 3 (1,3,5) | 3 (1,2,4) |
| $K_C$ | 1.10 | 1.19 | 1.43 | 1.35 | 1.14 | 0.80 | 1.30 |
| $n$ | 4 (1,2,4,5) | 4 (1,2,3,5) | 4 (1,2,3,4) | 5 | 6 | | |
| $K_C$ | 0.88 | 0.88 | 1.69 | 1.14 | 0.63 | | |
| 24. | Iodine–fluorobenzene in $CCl_4$ at 21°[s] | | | | | | |
| $n$ | 0 | 1 | 2 (1,3) | 3 (1,3,5) | | | |
| $K_N$ | 1.59 | 0.67 | 0.28 | 0.10 | | | |
| 25. | Iodine–fluorobenzene in heptane at 21°[s] | | | | | | |
| $n$ | 0 | 1 | 2 (1,3) | | | | |
| $K_N$ | 1.23 | 0.34 | 0.10 | | | | |
| 26. | Iodine monochloride–ethylbenzene in $CCl_4$ at 25°[e,f] | | | | | | |
| $n$ | 0 | 1 | 2 (1,3) | 3 (1,3,5) | 3 (1,2,4) | 4 (1,2,3,5) | 4 (1,2,4,5) |
| $K_G$ | 0.54 | 0.88 | 1.46 | 3.28 | 2.36 | 3.26 | 3.09 |

[a] $n$ = number of substituents; the location of substituents is given in parentheses where required. $K_C$ = concentration equilibrium constants in liter mole$^{-1}$; $K_K$ = equilibrium constants in mole fraction of Kg solvent mole$^{-1}$; $K_N$ = equilibrium constants in mole fraction. [b] R. M. Keefer and L. J. Andrews, *J. Am. Chem. Soc.*, **72,** 4677 (1950). [c] R. M. Keefer and L. J. Andrews, *ibid.*, **74,** 4500 (1952). [d] M. Tamres, D. R. Virzi, and S. Searles, *ibid.*, **75,** 4358 (1953). [e] R. M. Keefer and L. J. Andrews, *ibid.*, **72,** 5170 (1950). [f] N. Ogimachi, L. J. Andrews, and R. M. Keefer, *ibid.*, **77,** 4202 (1955). [g] R. D. Whittaker and H. H. Sisler, *J. Phys. Chem.*, **67,** 523 (1963). [h] L. J. Andrews and R. M. Keefer, *J. Am. Chem. Soc.*, **73,** 4169 (1951). [i] G. Briegleb and J. Czekalla, *Z. Elektrochem.*, **59,** 184 (1955). [j] R. Foster and C. A. Fyfe, *Trans. Faraday Soc.*, **61,** 1626 (1965). [k] N. B. Jurinski and P. A. D. de Maine, *J. Am. Chem. Soc.*, **86,** 3217 (1964). [l] R. Foster, D. L. Hammick, and B. N. Parsons, *J. Chem. Soc.*, 555 (1956). [m] M. W. Hanna and A. L. Ashbaugh, *J. Phys. Chem.*, **68,** 811 (1964). [n] L. L. Ferstandig, W. G. Toland, and C. D. Heaton, *J. Am. Chem. Soc.*, **83,** 1151 (1961). [o] R. E. Merrifield and W. D. Philips, *ibid.*, **80,** 2781 (1958). [p] L. J. Andrews and R. M. Keefer, *ibid.*, **71,** 3644 (1949). [q] L. J. Andrews and R. M. Keefer, *ibid.*, **72,** 5034 (1950). [r] N. Ogimachi, L. J. Andrews, and R. M. Keefer, *ibid.*, **78,** 2210 (1956). [s] M. Tamres, *J. Phys. Chem.*, **68,** 2621 (1964).

TABLE II

RESULTS OF CORRELATION WITH EQUATION 1

| Set | $b$ | $d$ | $r$[a] | $s$[b] | $s_b$[c] | $t$[d] | $n$[e] | cl[f] |
|---|---|---|---|---|---|---|---|---|
| 1 | 0.169 | 0.00770 | 0.996 | 0.0165 | 0.00924 | 18.33 | 5 | 99.9 |
| 2 | 0.168 | −0.847 | 0.951 | 0.112 | 0.0206 | 8.179 | 9 | 99.9 |
| 3 | 0.0158 | 0.228 | 0.993 | 0.0497 | 0.0108 | 14.65 | 5 | 99.9 |
| 4 | 0.251 | 0.669 | 0.991 | 0.0352 | 0.0197 | 12.75 | 5 | 99.0 |
| 5 | 0.257 | −0.322 | 0.973 | 0.125 | 0.0230 | 11.21 | 9 | 99.9 |
| 6 | 0.208 | −0.136 | 0.976 | 0.0704 | 0.0231 | 9.016 | 6 | 99.9 |
| 7 | 0.176 | −0.437 | 0.984 | 0.0670 | 0.0145 | 12.17 | 6 | 99.9 |
| 8 | 0.229 | −0.313 | 0.984 | 0.0485 | 0.0210 | 10.90 | 5 | 99.0 |
| 9 | 0.246 | −0.611 | 0.998 | 0.0386 | 0.00801 | 30.72 | 5 | 99.9 |
| 10 | 0.158 | −0.547 | 0.994 | 0.0401 | 0.0758 | 11.87 | 7 | 99.9 |
| 11 | 0.257 | −0.823 | 0.986 | 0.0906 | 0.0217 | 22.16 | 6 | 99.9 |
| 12 | 0.240 | −0.938 | 0.985 | 0.0888 | 0.0212 | 11.31 | 6 | 99.9 |
| 12A | 0.269 | −1.07 | 0.992 | 0.0632 | 0.0200 | 13.45 | 5 | 99.9 |
| 13 | 0.0869 | −0.411 | 0.767 | 0.152 | 0.0363 | 2.393 | 6 | 90.0 |
| 13A | 0.147 | −0.690 | 0.980 | 0.0550 | 0.0174 | 8.431 | 5 | 99.0 |
| 14 | 0.162 | −0.896 | 0.936 | 0.127 | 0.0305 | 5.323 | 6 | 99.0 |
| 14A | 0.207 | −1.10 | 0.979 | 0.0785 | 0.0248 | 8.338 | 5 | 99.0 |
| 15 | 0.102 | −0.839 | 0.983 | 0.0449 | 0.00849 | 12.07 | 7 | 99.9 |
| 15A | 0.115 | −0.895 | 0.995 | 0.0239 | 0.00572 | 20.16 | 6 | 99.9 |
| 16 | 0.147 | −0.940 | 0.941 | 0.127 | 0.0306 | 4.809 | 5 | 98.0 |
| 16A | 0.180 | −1.15 | 0.976 | 0.0895 | 0.0302 | 6.272 | 4 | 95.0 |
| 17 | 0.267 | −1.48 | 0.971 | 0.157 | 0.0379 | 7.043 | 5 | 99.0 |
| 18 | 0.274 | −0.120 | 0.992 | 0.0847 | 0.0160 | 17.11 | 7 | 99.9 |
| 19 | 0.212 | −1.32 | 0.986 | 0.0741 | 0.0136 | 15.59 | 9 | 99.9 |
| 20 | 0.227 | 0.481 | 0.973 | 0.0559 | 0.0313 | 7.268 | 5 | 99.0 |
| 21 | 0.374 | 0.168 | 0.994 | 0.0879 | 0.0162 | 23.10 | 9 | 99.9 |
| 22 | −0.0291 | 0.460 | 0.354 | 0.0888 | 0.0385 | 0.758 | 6 | 50.0 |
| 23 | −0.0309 | 0.130 | 0.439 | 0.113 | 0.0200 | 1.544 | 12 | 80.0 |
| 24 | −0.298 | 0.141 | 0.990 | 0.0897 | 0.0303 | 9.834 | 4 | 98.0 |
| 25 | −0.545 | 0.0854 | 0.9999 | 0.0110 | 0.00778 | 70.04 | 3 | 99.0 |
| 26 | 0.201 | −0.237 | 0.965 | 0.0906 | 0.0245 | 8.221 | 7 | 99.9 |
| 26A | 0.265 | −0.301 | 0.989 | 0.0630 | 0.0282 | 9.398 | 4 | 98.0 |
| 26B | 0.201 | −0.237 | 0.964 | 0.101 | 0.0277 | 7.243 | 6 | 99.0 |
| 26C | 0.276 | −0.313 | 0.995 | 0.0480 | 0.0131 | 20.99 | 6 | 99.9 |

[a] Correlation coefficient. [b] Standard error of the estimate. [c] Standard error of $b$. [d] "Student" t test. [e] Number of points in set. [f] Confidence level.

TABLE III

COMPARISON OF $b$ AND $d$ FROM EQUATIONS 1 AND 12

| Set (no.)[a] | $b_{12}$ | $b_1$ | $d_{12}$ | $d_1$ |
|---|---|---|---|---|
| 2 (5) | 0.111 | 0.168 | −0.825 | −0.847 |
| 4 (2) | 0.211 | 0.251 | 0.688 | 0.669 |
| 5 (3) | 0.194 | 0.257 | −0.259 | −0.322 |
| 18 (10) | 0.250 | 0.274 | −0.136 | −0.120 |
| 20 (9) | 0.193 | 0.227 | 0.475 | 0.481 |
| 21 (8A) | 0.270 | 0.374 | 0.305 | 0.168 |
| 25 | −0.504 | −0.545 | 0.0854 | 0.0413 |

[a] Set numbers in parentheses refer to Table III of the first paper of this series. Subscripts of $b$ and $d$ refer to the equations from which they were obtained. Values of $b_1$ and $d_1$ are from Table II of this paper.

TABLE IV

| $X^1X^2$ | H,H | H,F | F,F (1,3) |
|---|---|---|---|
| $K_N$ | 1.23 | 0.34 | 0.10 |

| $X^1X^2$ | F,Me (1,2) | F,Me (1,3) | F,Me (1,4) | H,Me |
|---|---|---|---|---|
| $K_N$ | 0.79 | 0.65 | 0.74 | 1.75 |

including the statistical factor for the tetraethylbenzenes, set 26C. The results for the latter set are by far the best. Furthermore, $b$ for set 26C is essentially the same as $b$ for set 26A which we judge from the models to be free of steric effects. We conclude that the use of the statistical factor is justified in the case of the tetraethylbenzenes. It seems reasonable to apply this argument to any polysubstituted benzene donor in which inspection of models shows one side of the ring incapable of complex formation and the other side unhindered.

**Acknowledgment.**—The author acknowledges the use of the facilities of the Computer Laboratories, School of Engineering and Science, Pratt Institute.

# Copper Salts Catalyzed Addition of Trichloro- and Dichloroacetonitriles to Olefins

SHINJI MURAI AND SHIGERU TSUTSUMI

*Department of Chemical Technology, Faculty of Engineering, Osaka University, Miyakojima-ku, Osaka, Japan*

*Received October 22, 1965*

The copper salts catalyzed addition of trichloro- and dichloroacetonitriles to olefins gives good yields of 1:1 adducts. From 1-octene, 1-hexene, styrene, ethyl acrylate, methyl acrylate, and acrylonitrile, 4-substituted 2,2,4-trichloro- and 2,4-dichlorobutyronitriles are prepared. From norbornene, 1:1 adducts are also obtained.

Peroxide-induced additions of alkyl polyhalides to olefins are well known.[1] Recently additions of carbon tetrachloride,[2a–f] chloroform,[2a,b,d,g] N-chloroamines,[3] and sulfonyl chlorides[4] to olefins using catalytic amounts of copper or iron salts were reported and an oxidation–reduction mechanism was suggested for these reactions. In these "oxidation–reduction additions," chain transfer occurs on the metallic ion of higher oxidation state and this suppresses the telomerization almost completely and therefore the use of a large excess of organic halide is unnecessary. Hence this oxidation–reduction addition reaction is of great importance as a synthetic tool. Moreover, it is worth noting that the adducts of chloroform and olefins are 1,1,3-trichloroalkanes, as distinguished from 1,1,1-trichloroalkanes which are the products of peroxide-catalyzed reactions as reported by Minisci and Galli[2a,b] and also by Asscher and Vofsi.[2d,g]

It has previously been shown in this laboratory that ethyl trichloroacetate can also be added to olefins in the presence of a catalytic amount of copper salts.[5] In a further effort to prepare polychloroalkanes having important substituents, the copper salts catalyzed reactions between polychloroacetonitriles and olefins were investigated. Experiments described in this paper show that, by the reaction of trichloro- and dichloroacetonitriles with various olefins, 2,2,4-trichloro- and 2,4-dichlorobutyronitriles were obtained in good yields. The results are summarized in Tables I and II. In the reactions of ethyl acrylate and methyl acrylate, small amounts of 2:1 adducts were formed as well as the 1:1 adducts.

In a typical experiment, a mixture of an olefin (0.1 mole), a polychloroacetonitrile (0.1 mole), a copper salt (0.002 mole), and acetonitrile (50 ml) was heated at 130–140° for 18 hr in a sealed-glass tube in an oil bath. Afterwards solvent and unchanged materials were removed *in vacuo* and precipitated inorganic material were removed by filtration. Then the 1:1 adduct was distilled within a very narrow boiling point range. No significant amount of polymeric residue was left.

A wide range of catalysts was employed in the reaction of 1-octene with trichloroacetonitrile. When either CuCl, CuBr, CuCN, CuSCN, $Cu_2O$, CuS, $CuCl_2$, or $Cu(OAc)_2H_2O$ was used, the yield of 1:1 adduct was essentially the same (73–83%). Copper powder or ferrous chloride tetrahydrate was also an effective catalyst, but gave lower yields of 1:1 adduct. When the reaction of 1-octene with trichloroacetonitrile was carried out in the presence of cuprous chloride for 24 hr in refluxing acetonitrile (*ca.* 80°), the yield of 1:1 adduct was only 16%. In the reactions with olefins

---

(1) (a) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p 247; (b) C. Walling and E. S. Huyser, *Org. Reactions*, **13**, 91 (1963).

(2) (a) F. Minisci and R. Galli, *Tetrahedron Letters*, 533 (1962); (b) M. De Male, F. Minisci, E. Volterra, and A. Quilico, *Chim. Ind.* (Milan), 371 (1956); (c) M. Asscher and D. Vofsi, *J. Chem. Soc.*, 2261 (1961); (d) M. Asscher and D. Vofsi, *Chem. Ind.* (London), 209 (1963); (e) M. Asscher, E. Levy, H. Rosin, and D. Vofsi, *Ind. Eng. Chem., Prod. Res. Develop.*, **2**, 121 (1963); (f) M. Asscher and D. Vofsi, *J. Chem. Soc.*, 1887 (1963); (g) M. Asscher and D. Vofsi, *ibid.*, 3921 (1963).

(3) F. Minisci and R. Galli, *Tetrahedron Letters*, 167 (1964); 546 (1964); 3179 (1964); *Chim. Ind.* (Milan), **45**, 1400 (1963).

(4) M. Asscher and D. Vofsi, *Chem. Ind.* (London), 32 (1964); *J. Chem. Soc.*, 4962 (1964).

(5) S. Murai, N. Sonoda, and S. Tsutsumi, *J. Org. Chem.*, **29**, 2104 (1964).