are the major reaction paths in the acetolysis of the *cis*-2-halocyclohexyl *p*-bromobenzenesulfonates.

TABLE I

FIRST-ORDER ACETOLYSIS RATE CONSTANTS OF 2-SUBSTITUTED CYCLOHEXYL *p*-BROMOBENZENESULFONATES, 74.9°

2-Substituent	$ROSO_2C_6H_4Br$ *m*	$KOC_8H_5O_3$[a] *m*	10^8 *k*, sec.$^{-1}$
trans-Cl	0.0393	....	5.97[b]
	.0736	....	5.94
	.0434	0.0168	6.3[c]
cis-Cl	.0392	....	1.58
	.0778	....	1.58
	.0470	.0168	2.32
cis-Br	.0446	....	1.51
	.0723	....	1.58
	.0481	.0167	2.58
trans-Br[d]	.05	....	1250

[a] $KOC_8H_5O_3$, potassium acid phthalate. [b] Previous value[2] 5.64. [c] Extrapolated value at zero time. [d] Data taken from reference 2.

Experimental

Materials.—*cis*-2-Chlorocyclohexyl *p*-bromobenzenesulfonate, m.p. 93–94°, *trans*-2-chlorocyclohexyl *p*-bromobenzenesulfonate, m.p. 79–80°, and *cis*-2-bromocyclohexyl *p*-bromobenzenesulfonate, m.p. 95.4–95.6°, were prepared and furnished by Dr. R. B. Loftfield. The syntheses will be described by him elsewhere.

Glacial acetic acid, acetic anhydride, and potassium acid phthalate were reagent grade chemicals.

Rate Measurements.—The sealed ampoule technique of rate measurement described previously[2] was used. Titrations were done with perchloric acid or potassium acid phthalate in glacial acetic acid to brom phenol blue[2] or tropaolin 00 indicator. Rates were followed to about 10% reaction, and over this range the kinetics was first order within the experimental error of 5% for the *cis*-2-haloesters. For the acetolysis of *trans*-2-chlorocyclohexyl *p*-bromobenzenesulfonate in the absence of potassium acid phthalate, first-order kinetics was observed within the experimental error of 5%, but the end-points of the titration were not very sharp and reaction mixtures to which a slight excess of potassium acid phthalate was added turned neutral in a few minutes due to some secondary reaction. Acetolysis of *trans*-2-chlorocyclohexyl *p*-bromobenzenesulfonate in the presence of 0.017 *m* potassium acid phthalate proceeded with complicated kinetics. Calculated first-order rate constants increased during the reaction, as is illustrated in Table III, again presumably due to a consecutive reaction involving acetate. The specific rate listed in Table I was obtained by extrapolation to zero time.

TABLE II

PREDICTED VALUES OF k_C FOR THE 2-HALOCYCLOHEXYL *p*-BROMOBENZENESULFONATES, 74.9°

2-Substituent	*W*, kcal./mole[a]	$k_C \times 10^8$, sec.$^{-1}$	$k \times 10^8$, sec.$^{-1}$
trans-Cl	(5.30)[a]	(5.9)	5.9
cis-Cl	8.03	0.11	1.58
trans-Br	4.90	10.4	1250
cis-Br	7.36	0.30	1.55

[a] The value of the parameter M_1/D_E was obtained from the data for *trans*-2-chlorocyclohexyl *p*-bromobenzenesulfonate. $W = RT \ln (k_H/k_C)$, as in reference 2.

TABLE III

ACETOLYSIS OF *trans*-2-CHLOROCYCLOHEXYL *p*-BROMOBENZENESULFONATE IN THE PRESENCE OF 0.0168 *m* POTASSIUM ACID PHTHALATE, 74.9°

Time, hr.	$ROSOOC_6H_4Br$, *m*	$KOC_8H_5O_3$, *m*	10^8 *K*,[a] sec.$^{-1}$
0.0	0.04345	0.01676	(6.3)
89.5	.04255	.01586	6.49
267.5	.04068	.01399	6.84
476.0	.03838	.01169	7.24
767.7	.03464	.00795	8.20
976.3	.03234	.00565	8.40

[a] $K = [\ln a/(a - x)]/t$.

Calculation of *W*.—Study of Fisher–Taylor–Hirshfelder models revealed that electron attracting *trans*-1,2-cyclohexane substituents choose only the polar-*trans* positions of the chair form of cyclohexane[7] where they are nearly coplanar with their carbon atoms and oriented *trans*. In this way the dipole-interaction energies *W* are minimized. For two electron-attracting *cis*-substituents, there seems little to choose between the 1,2-positions in either the chair-form or the boat-form of cyclohexane. The angles and distances for all possible positions appear to be very comparable. Also, at the angles and distances typical of *cis*-1,2-substituents, the interaction energy *W* is not very sensitive to small changes in geometry. Therefore, it seemed logical to compute *W* for *cis*-bromine and *cis*-chlorine neighboring groups using the same model as before,[2] *i.e.*, a model where the *trans*-bonds are coplanar.

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[7] R. C. Fuson and H. R. Snyder, "Organic Chemistry," John Wiley and Sons, New York, N. Y., 1942, p. 14.

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The Partial Molal Entropy of Cuprous Ion

BY Z. Z. HUGUS, JR.

The Bureau of Standards tables[1] give as the partial molal entropy of cuprous ion, −6.3 e.u. Such a value seems too negative in view of the known entropies of other plus one ions.[2]

Apparently the literature contains only two determinations of equilibrium in the reaction

$$Cu(c) + Cu^{++} = 2Cu^{+}$$

over a range of temperatures. Kawassiadis[3] studied this equilibrium in sulfate solutions in the temperature range 50–200°. His results when plotted as $-R \ln K$ against $1/T$ seem erratic, and have been discarded as unreliable. Heinerth[4] studied the same equilibrium in sulfate and perchlorate solutions in the temperature range 20–60°. He found that variation in cupric concentration caused no change within experimental error in the quotient $(Cu^{++})^{1/2}/(Cu^{+})$. Thus it appeared that the activity coefficients of cuprous and cupric ions tended to cancel. Heinerth regarded his results in perchlorate solutions as uncertain since there was evidence that perchlorate was reduced, and with this in mind only his results in sulfate solution have been taken into account.

From Heinerth's data one may calculate for the above reaction

$$\Delta F^{\circ}_{298} = +8.29 \text{ kcal.}$$

and

$$\Delta H_{298} = +18.78 \text{ kcal.}$$

the uncertainty in these values being ±0.1 kcal. Using the known entropies of Cu(c), 7.97 e.u.

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[1] Selected Values of Chemical Thermodynamic Properties, Series I, National Bureau of Standards, Washington, D. C. (1947, *et seq.*).

[2] See for example, K. K. Kelley, U. S. Bur. Mines Bull., No. 477 (1950).

[3] C. T. Kawassiadis, *Praktika Akad. Athenon*, **10**, 391 (1935).

[4] E. Heinerth, *Z. Elektrochem.*, **37**, 61 (1931).

and Cu^{++}, −26.5 e.u.[2] the value $S^\circ_{Cu^+} = +8.3 \pm 2.0$ e.u. is found.

In view of the relation of Powell and Latimer[5] connecting the ionic radii and the partial molal entropies of aqueous ions this value seems more reasonable than the Bureau of Standards value.

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(5) R. E. Powell and W. M. Latimer, *J. Chem. Phys.*, **19**, 1139 (1951).

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The "Carbonyl" Frequency in Polycyclic Quinones

BY D. HADŽI AND N. SHEPPARD

In a recent communication Josien and Fuson[1] have pointed out that the "carbonyl" frequency in some polycyclic compounds, mainly quinones, has an abnormally low value in the infrared spectrum (*e.g.*, 6.1 μ or approximately 1640 cm.$^{-1}$ for 3,8- and 3,10-pyrenequinone). In connection with some work on coking substances and coal extracts, we have also studied the infrared spectra of a series of polynuclear quinones and some related hydrocarbons. A selection of the "carbonyl" frequencies that have been obtained in Nujol mulls of the quinones are listed below and may be compared with the values of 1660 cm.$^{-1}$ (6.01 μ) for *p*-benzoquinone and 1676 cm.$^{-1}$ (5.97 μ) for anthraquinone, obtained previously by Flett.[2]

	cm.$^{-1}$	μ
p-Naphthoquinone	1664	6.01
Pyranthrone	1655	6.04
Mesonaphthadianthrone	1649	6.06
Helianthrone	1646	6.08
1,2:6,7-Dibenzpyrene-3,8-quinone	1645	6.08
Dibenzanthrone	1638	6.10
Diphenoquinone	1626	6.16

It can be seen that the "carbonyl" frequencies of the polynuclear quinones listed above vary considerably in value. Taking into account these results and those of the earlier workers[1,2] it appears that paraquinones in which the two quinone carbonyl groups occur in the same ring absorb in the range 1660 to 1680 cm.$^{-1}$, and that extended quinones, in which the carbonyl groups are in different rings, usually absorb in the range 1635 to 1655 cm.$^{-1}$. In confirmation of this latter point we have found that benzanthrone has its "carbonyl" band at 1644 cm.$^{-1}$, and anthrone has been shown previously to absorb at 1654 cm.$^{-1}$ [2]; both of these molecules have single carbonyl groups coupled in a similar fashion to polycyclic ring systems. A single exception to the above rule concerning the "carbonyl" frequencies of extended quinones is provided by diphenoquinone. However this result may be abnormal on account of the unusual structure and chemical properties of this molecule. In any case the above correlations must only be considered as provisional and as subject to refinement when the spectra of a more extensive series of molecules of this type become available. Other quinone type molecules for which we have observed low "carbonyl" frequencies are 3,3′- and 4,4′-dibenzanthronyl (1626 and 1630 cm.$^{-1}$, respectively). An insufficient number of orthoquinones seem to have been studied spectroscopically to enable correlation rules to be drawn up at present.

In picking out the "carbonyl" frequencies we have listed the strong absorption band for each compound which lies at the highest frequency in the region 1550 to 1750 cm.$^{-1}$. It is of interest to note however that in some cases other equally strong absorption bands occur in the infrared spectra in the region 1570 to 1600 cm.$^{-1}$.[3] As the skeletal vibrations of polycyclic ring systems often occur in this range[4] it seems probable that, as might be expected, several of these modes of vibration also involve considerable vibrational motion of the carbonyl linkages. This coupling with ring skeletal vibrations would explain at the same time the high intensity of these lower frequency absorption bands and the variable nature of the so-called carbonyl frequency itself. In all cases that we have so far investigated only very much weaker bands are found in the region 1550–1750 cm.$^{-1}$ for the corresponding hydrocarbons.

On further comparison of the spectra of the quinones and related hydrocarbons, differences were also found in the regions of the spectra which are not close to the "carbonyl" frequency. Thus in the spectra of the quinones strong absorption bands were found in region 1200–1350 cm.$^{-1}$ which are not present in comparable strength in the hydrocarbon spectra, and presumably also arise from the coupling of the C=O vibration with those of the rest of the molecule. In addition the features in the spectra of the quinones and hydrocarbons between 900 and 700 cm.$^{-1}$ which can usually be attributed to the out-of-plane vibrations of the CH linkages attached to the aromatic skeleton[4] also showed considerable differences as would be expected from the changes in substitution pattern. Further spectroscopic work on these types of molecules is continuing.

We are very grateful to Professor A. R. Todd, F.R.S. and Dr. A. W. Johnson of the University Chemical Laboratory, Cambridge, and to Imperial Chemical Industries (Dyestuffs), Ltd., for samples of the substances studied.

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(1) M. L. Josien and N. Fuson, THIS JOURNAL, **73**, 478 (1951).

(2) M. St. C. Flett, *J. Chem. Soc.*, 1441 (1948).

(3) A similar effect has been noted previously as being caused by the conjugation of a C=O group to a phenyl ring (Randall, Fowler, Fuson and Dangl, "Infra-red Determination of Organic Structures," D. Van Nostrand and Co., New York, N. Y., 1949, p. 16).

(4) S. F. D. Orr and H. W. Thompson, *J. Chem. Soc.*, 218 (1950).

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Viscosity of Polytrifluorochloroethylene in o-Chlorobenzotrifluoride

BY H. TRACY HALL, EDWARD L. BRADY AND PAUL D. ZEMANY

Viscosity data for polytrifluorochloroethylene in a chlorofluorobutane solvent have been presented by H. S. Kaufman and M. S. Muthana.[1] We

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(1) Paper No. 26, Division of High Polymer Chemistry, American Chemical Society Meeting, September 5, 1950.