TABLE II

THE INTERACTION COEFFICIENTS OF THE GAS MIXTURES AT 30°

Mixture	ϵ_0/k, °K.	r_0, Å.	B_{11}	B_{22}	B_{12} Calcd.	B_{12} Detd.
CO_2–N_2	185, 95.9	4.57, 3.72	−120.7	− 4.34	−39.1	−40.6 ± 0.2
CO_2–O_2	185, 117.5	4.57, 3.58	−120.7	−15.96	−49.9	−41.5 ± .2
O_2–N_2	117.5, 95.9	3.58, 3.72	−15.96	− 4.34	−10.1	− 9.7 ± .3

N_2–O_2 system show definitely that the interaction coefficient even for this pair is not the arithmetic mean of the virial coefficients for the separate constituents.

The Table I values for the CO_2–O_2 mixtures are in good agreement among themselves, showing no large effects of interchange of the placements of the gases in the apparatus. The large discrepancy between the two B_{12} values shown in Table II for this mixture is difficult to explain. It does not appear to be caused by experimental error or by error in the theory of Edwards and Roseveare.[6] The molar value of $\Delta V/x_1x_2$ corresponding to B_{12} calcd. would be only 36.61 cc.

Efforts to get better agreement between B_{12} calcd. and B_{12} detd. for the CO_2–O_2 system by a different choice of the force constants failed. Values chosen from viscosity data[2] and use of the 0–200° values given by MacCormack and Schneider[7] for carbon dioxide gave no improvement. It is possible that the cause of the difficulty is the set of combination rules used to obtain the parameters for the computation of B_{12} calcd.

Edwards and Roseveare are the only other workers who have determined B_{12} for the CO_2–O_2 system. Using their $\Delta V/x_1x_2$ value measured at 25° and the force constants of Table II, we obtain a B_{12} detd. value of −58.3 cc. mole^{-1}, while B_{12} calcd. comes to −52.1 cc. mole^{-1} at this temperature. Their high value of B_{12} detd. may be due to experimental error. The comparisons made by Lunbeck and Boerboom[5] indicate that the ΔV values obtained by Edwards and Roseveare in their pioneering work are generally too low.

Acknowledgment.—It is a pleasure to acknowledge the aid of the Bureau of Ships and the Office of Naval Research, both of the Navy Department, who have sponsored this work. The assistance of Dr. J. A. Goff, C. Nocka, S. Voltz and V. Folen in the preliminary stages of this study is also gratefully acknowledged.

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[6] A novel test of the method was made for the CO_2–O_2 system by mixing one of the pure gases with a prepared mixture of both. This was done by flushing the whole apparatus with one of the gases and filling with this gas to a pressure of one-half atmosphere. The second of the two gases was then added to flask A while at the same time the first gas was used to complete the filling of flask B until the pressure balance was obtained at one atmosphere. The approximately equimolecular mixture of the two gases in flask A was then mixed with the pure gas in flask B, the resultant volume change, ΔV, being measured in the usual manner. For this case it can be shown, with the same assumptions as made in the derivation of equation (4), for the mixing of pure gases, that

$$\Delta V = (n_1 + n_2' + n_2)^{-1}\,[n_1^2B_{11} + 2n_1(n_2' + n_2)B_{12} + (n_2' + n_2)^2B_{22}] - n_2B_{22} - (n_1 + n'_2)^{-1}[n_1^2B_{11} + 2n_1n_2'B_{12} + n_2'^2B_{22}]$$

where n_1 is the number of moles of gas 1 in flask A, while n_2' and n_2 are the numbers of moles of gas 2 in flask A and flask B, respectively, before the mixing which produces the measured volume change at constant temperature and pressure. Two experiments of this type were carried out at 30°. In the one, pure oxygen was mixed with a mixture of oxygen and carbon dioxide; in the other, pure carbon dioxide was mixed with the mixture. The values of B_{12} determined for the CO_2–O_2 system in this way, using the same B_{11} values as given in Table II, were −41.9 and −41.6 cc. per mole, respectively.

[7] K. E. MacCormack and W. G. Schneider, *J. Chem. Phys.*, **19**, 849 (1951).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY OF IOWA]

Solutions of Halogens in Highly Acidic, Polar Solvents[1]

BY ROBERT E. BUCKLES AND JACK F. MILLS

RECEIVED AUGUST 4, 1952

A study of the absorption spectra of iodine, iodine chloride and bromine in various solvents showed that in the highly acidic, polar solvents, trifluoroacetic acid and sulfuric acid, the halogens behaved spectrophotometrically very much as they did in relatively non-polar solvents, *e.g.*, carbon tetrachloride or ethylene chloride, where little if any complexing is expected to take place. On the other hand a comparison of the halogens in these very acidic solvents with solutions in anhydrous acetic acid, a typical complexing solvent for halogens, showed much wider spectrophotometric differences. Estimation of equilibrium constants for the complexing of iodine and iodine chloride with acetic acid and with trifluoroacetic acid also showed that the latter highly acidic solvent has considerably less tendency to complex than does the former less acidic solvent.

Recent studies[2] of the 1:1 complexes formed between halogens and aromatic compounds or compounds containing oxygen, nitrogen or iodine have led to the opinion that the halogen molecule acts as a generalized acid or acceptor of the available electrons of the generalized base with which it complexes. This view of the colors observed in such solvents as compared with those observed in relatively non-complexing solvents has been preferred to alternative explanations[3] involving polarization of the halogen molecules by the solvent mole-

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[1] Work carried out under Contract No. AT(11-1)-72, Project No. 7 with the U. S. Atomic Energy Commission. Presented before the Division of Physical and Inorganic Chemistry of the American Chemical Society, Atlantic City, N. J., September, 1952. Abstracted from the Ph.D. thesis of Jack F. Mills.

[2] (a) J. Kleinberg and A. W. Davidson, *Chem. Revs.*, **42**, 601 (1948); (b) H. A. Benesi and J. H. Hildebrand, THIS JOURNAL, **70**, 2382 (1948); **71**, 2703 (1949); (c) R. S. Mulliken, *ibid.*, **72**, 600 (1950); **74**, 811 (1952); (d) R. M. Keefer and L. J. Andrews, *ibid.*, **72**, 4677, 5170 (1950); **73**, 462 (1951); **74**, 458, 1891 (1952); (e) T. M. Cromwell and R. L. Scott, *ibid.*, **72**, 3825 (1950).

[3] (a) S. Freed and K. M. Sancier, *ibid.*, **74**, 1273 (1952); (b) N. S. Bayliss, *J. Chem. Phys.*, **18**, 292 (1950).

cules. It is true that dissociation into ions has been reported[4] in some of these cases where the characteristic color of the uncomplexed halogen has been observed to change when a complexing substance was added, but such results merely demonstrate the ability of the complexes, themselves, to dissociate into ions.

The present work gives further evidence in support of the donor–acceptor view of the complexing of halogens with solvent.

Experimental

Halogens and Solvents.—Resublimed, analytical grade iodine, m.p. 113–114°, was used in the preparation of stock solutions. Iodine chloride,[5] m.p. 27–28°, was allowed to sublime from the bottom of the glass-stoppered bottle in which it was stored onto the walls of the bottle. These freshly sublimed crystals were then used for making stock solutions. Bromine was purified by treatment with potassium bromide and barium oxide as described by Bauer and Daniels[6] but the product of the final distillation was not recrystallized.

Commercial ethylene chloride (Carbide and Carbon) was washed with concentrated sulfuric acid followed by several portions of water. Most of the water was removed by distillation of the azeotrope (8.9% water). Distillation from phosphorus pentoxide through a 30-inch helices-packed column yielded a product of b.p. 83.0–83.1° (745 mm.) which was generally stable to the halogens used under the conditions of the measurements. Carbon tetrachloride was shaken with warm concentrated aqueous potassium hydroxide and alcohol, followed by water and then concentrated sulfuric acid as described by Fieser.[7] After a final wash with water the organic layer was dried over calcium chloride and distilled from phosphorus pentoxide to yield a product of b.p. 76.7–76.8° (745 mm.).

Glacial acetic acid was boiled with acetyl borate under reflux for one hour and then distilled to give a product of b.p. 118.0–118.1° (745 mm.) and m.p. 16.7°.[8] Trifluoroacetic acid (Minnesota Mining and Manufacturing Company) was boiled with phosphorus pentoxide under reflux for one hour. Distillation from fresh phosphorus pentoxide yielded a product of b.p. 71.1–71.2° (745 mm.). Concentrated sulfuric acid (96%) was distilled at reduced pressure before being used for stock solutions.

Methods of Analysis.—Solutions of halogens in ethylene chloride or carbon tetrachloride were analyzed iodometrically. A magnetic stirrer was used during the determinations to ensure equilibrium between the phases. Solutions of halogens in acetic acid or trifluoroacetic acid were simply diluted with water and the halogen concentration was determined iodometrically. In the case of trifluoroacetic acid, however, it was essential that at least a 10 to 1 dilution with water was used.

Solutions of halogen in concentrated sulfuric acid were quantitatively extracted with several portions of carbon tetrachloride. The amount of halogen in the combined extracts was determined iodometrically as described above. Results reproducible to within 1% were possible by this procedure.

Absorption Spectra.—For each series of measurements fresh stock solutions were prepared and standardized. Dilution of the stock solution to suitable concentrations was then carried out. Measurements were carried out at 25° in calibrated silica cells of path length 1.00 ± 0.01 and in a few cases in 2- and 5-cm. cells of comparable precision. The complete absorption spectra curves were measured on a Cary Model 11 recording spectrophotometer. The absorbancy measurements for equilibrium data were obtained with the Beckman DU and the Beckman Model B spectrophotometers. The uniform nomenclature and symbology suggested by the National Bureau of Standards[9] was used throughout this article.

Results and Discussion

In Table I are given the data for the absorption spectra peaks of iodine, iodine chloride and bromine in several solvents. Also the complete absorption spectra curves for carbon tetrachloride, acetic acid and trifluoroacetic acid solutions of each of the three halogens are given in Figs. 1, 2 and 3. As far as wave lengths are concerned, the absorption peaks of halogens in the highly acidic solvents are nearer those of the solutions where complexing is at a minimum than they are to those where complexing is appreciable. This is especially striking in the cases of iodine (Fig. 1) and iodine chloride (Fig. 2) where the differences are visible. In other words, trifluoroacetic acid or sulfuric acid are "violet" solvents for iodine while acetic acid is a "brown" solvent. As has been shown[3a,10] with other solvents the interaction of iodine and trifluoroacetic acid was exothermic. Strong cooling of the solution in a Dry Ice–ether-bath caused it to become quite brown. When warmed to room temperature its violet color returned. In the case of bromine (Fig. 3), complexing in acetic acid is especially exemplified by the large increase in the molar absorbancy index between 250 and 300 mμ which is not shown in trifluoroacetic acid, sulfuric acid, or non-complexing solvents in general. Such enhanced absorption in this region is characteristic of many of the halogen–solvent complexes recently studied.[2]

TABLE I

ABSORPTION PEAKS OF HALOGENS IN VARIOUS SOLVENTS

	I_2		ICl		Br_2	
Solvent	λ, mμ	a_m	λ, mμ	a_m	λ, mμ	a_m
CH_3COOH	478	775	362.5	138	400	181
CF_3COOH	515	655	450	105	411	138
H_2SO_4	502	770	442	143	405	157
$C_2H_4Cl_2$	500	890	426	131	411	206
CCl_4	517	918	460	152	417	203

Estimates of the equilibrium constants for complex formation in the case of the halogens interacting with acetic acid and trifluoroacetic acid in carbon tetrachloride were carried out. A spectrophotometric method similar to those used[2b,d] in other cases was developed. It was necessary to make measurements at wave lengths where uncomplexed halogen had an appreciable molar absorbancy index (extinction coefficient). It was assumed that this molar absorbancy index was approximately equal to that of the halogen in carbon tetrachloride. The equation for the reaction is given in equation (1) and the expression for its equilibrium constant is given by equation (2) where N_B is the mole fraction of solvent complexing with the halogen and the C's are concentrations in moles per liter.

$$X_2 + B = X_2B \qquad (1)$$

$$K = \frac{(X_2B)}{(X_2)\,(B)} = \frac{C_{X_2B}}{C_{X_2}N_B} \qquad (2)$$

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[4] (a) L. F. Audrieth and E. J. Birr, THIS JOURNAL, **55**, 668 (1933); (b) R. A. Zingaro, C. A. VanderWerf and J. Kleinberg, *ibid.*, **73**, 88 (1951); (c) R. E. Buckles and N. A. Meinhardt, *ibid.*, **74**, 1171 (1952).

[5] J. Cornog and R. A. Karges, *ibid.*, **54**, 1882 (1932).

[6] W. H. Bauer and F. Daniels, *ibid.*, **56**, 378 (1934).

[7] L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., New York, N. Y., 1941, p. 365.

[8] W. C. Eichelberger and V. K. La Mer, THIS JOURNAL, **55**, 3633 (1933).

[9] National Bureau of Standards Letter-Circular LC-857 (1947).

[10] A. Lachman, THIS JOURNAL, **25**, 50 (1903).

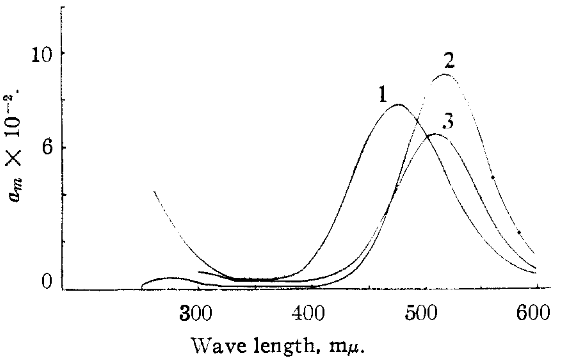

Fig. 1.—Absorption spectra of iodine in: 1, acetic acid (1.0×10^{-3} *M*, 2-cm. cell); 2, carbon tetrachloride (5×10^{-4} *M*, 1-cm. cell); 3, trifluoroacetic acid (2.5×10^{-3} *M* 5-cm. cell).

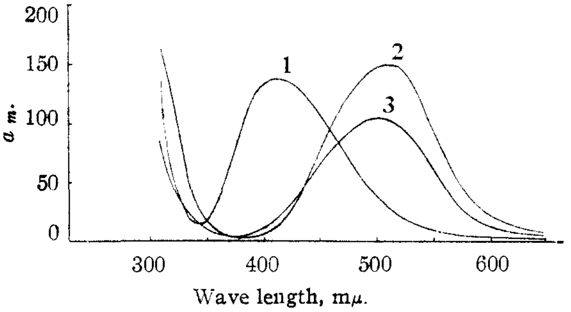

Fig. 2.—Absorption spectra of iodine chloride in: 1, acetic acid (1×10^{-2} *M*, 2-cm. cell); 2, carbon tetrachloride (4×10^{-3} *M*, 1-cm. cell); 3, trifluoroacetic acid (8×10^{-4} *M*, 1-cm. cell).

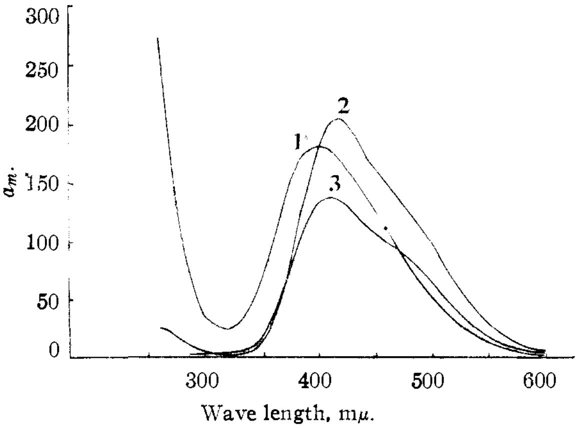

Fig. 3.—Absorption spectra of bromine in: 1 acetic acid (2.5×10^{-3} *M*, 1-cm. cell); 2, carbon tetrachloride (2×10^{-3} *M*, 1-cm. cell); 3, trifluoroacetic acid (1×10^{-2} *M*, 1-cm. cell).

The absorbancy (optical density) of the solution balanced against that of the mixed solvents is given by equation (3) where a_c is the molar absorbancy index of the complex, a_X is the molar absorbancy index of the uncomplexed halogen and b is the thickness of solution in the cell.

$$A_s = C_{X_2B}a_cb + C_{X_2}a_Xb \qquad (3)$$

The combination of equations (2) and (3) with equation (4), where C_t is the total halogen concentration, gives equation (5).

$$C_t = C_{X_2} + C_{X_2B} \qquad (4)$$

$$A_s = C_ta_cb + 1/K\,(C_ta_Xb - A_s/N_B) \qquad (5)$$

Plots of $(C_ta_Xb - A_s)/N_B$ against A_s then should give straight lines when constant total halogen concentrations are used.

The mole fraction of complexing solvent was based on the dimeric form for acetic acid[11] and trifluoroacetic acid[12]; however, there seemed to be no reason in the present work for assuming that the halogen complexes with the monomer.[13] In fact the results fit equation (5) much better for acetic acid if this assumption was not made, and if the complex was considered to be 1:1 between the dimer and halogen.

Plots for the determination of the equilibrium constants for the complexing of iodine chloride are given in Fig. 4. Similar results were obtained with iodine chloride at other concentrations and with iodine. Statistical estimation of the slopes and intercepts led to the following average values of K at 25° for complexing with acetic acid where the measure of the precision given is the standard deviation. For iodine K was 3.4 ± 0.3 and a_c was 886 at 478 mμ, and for iodine chloride K was 18.4 ± 0.7 and a_c was 146 at 362.5 mμ.

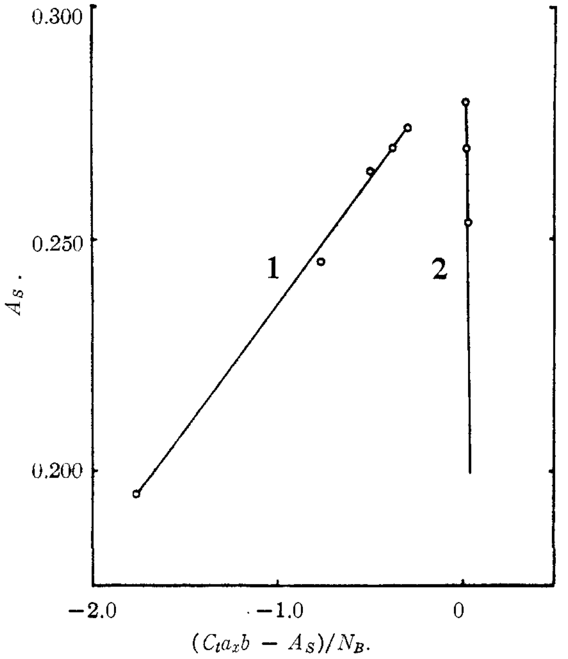

Fig. 4.—Plots of absorbancy data for iodine chloride in (1) acetic acid–carbon tetrachloride and (2) trifluoroacetic acid–carbon tetrachloride according to equation (5). Total halogen concentration in each case was 2×10^{-3}.

For the halogens with trifluoroacetic acid, it appears from the absorption spectra (Figs. 1, 2 and 3) that most of the absorption at the peak in each case is that of the uncomplexed halogen. The lower value for the molar absorbancy index at the peak in each case must be caused by interaction

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[11] L. Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1940, p. 307; M. Trautz and W. Moschel, *Z. anorg. Chem.*, **155**, 13 (1926).

[12] J. Karle and L. O. Brockway, THIS JOURNAL, **66**, 574 (1944).

[13] J. H. Hildebrand and B. L. Glascock, *ibid.*, **31**, 26 (1909).

of some sort with the solvent. The application of equation (5) to these cases even at the wave lengths of maximum absorbancy requires that the correction for the absorbancy of uncomplexed halogen be nearly as great as the absorbancy of the solution itself. The points obtained in such calculations were widely scattered, and lines of negative slope were often encountered. In all cases the values of the equilibrium constant for complexing were near zero with a high standard deviation whether they were negative or positive. It is certain that trifluoroacetic acid does interact with the halogens as shown in the absorption spectra, but the extent of the interaction cannot be measured accurately by this method. The equilibrium constant in the case of iodine and iodine chloride with trifluoroacetic acid was of the order of 0 ± 0.9 where 0.9 sets the 95% confidence limits of the values.

Inconclusive results were obtained with bromine in both acetic and trifluoroacetic acids. In the former case especially, it was necessary to use small differences of large absorbancy values in the calculations.

The highly polar trifluoroacetic acid (the dielectric constant is 42.1 at 25°[14] even though largely in the relatively non-polar dimeric form[12]) and 96% sulfuric acid (the dielectric constant is greater than 84 at 20°)[15] were evidently not nearly as effective in complexing with halogens as was the much less polar acetic acid (the dielectric constant is 6.13 at 20°).[16] It seems reasonable to conclude that the very structural features which make trifluoroacetic acid and sulfuric acid such strong proton donors would make them exceedingly weak electron donors. Consequently such solvents would not be expected to complex with halogens as well as more basic substances (*e.g.*, acetic acid) in spite of the fact that they are very polar in nature.

[14] J. H. Simons and K. E. Lorentzen, THIS JOURNAL, **72**, 1426 (1950).

[15] P. Walden, *Z. physik. Chem.*, **46**, 182 (1903).

[16] C. P. Smyth and H. E. Rogers, THIS JOURNAL, **52**, 1824 (1930).

IOWA CITY, IOWA

[CONTRIBUTION FROM THE COATES CHEMICAL LABORATORY, LOUISIANA STATE UNIVERSITY]

Oscillographic Polarographic Waves for the Reversible Deposition of Metals on Solid Electrodes

BY TALIVALDIS BERZINS AND PAUL DELAHAY

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An equation is derived for oscillographic polarographic waves corresponding to the reversible deposition of an insoluble substance. Theoretical results are compared with experimental data, and discrepancies are accounted for by variations of the activity of the deposit.

The following three major types of electrode processes should be considered in the development of the theory of oscillographic polarography: (1) electrode processes for which it can be assumed that electrochemical equilibrium is achieved between two soluble species; (2) reversible electrode processes yielding an insoluble substance; (3) irreversible electrode processes. The theoretical treatment of oscillographic waves corresponding to electrode processes of the first type was developed by Randles[1] and Sevcik.[2] The other two types of oscillographic waves were studied in this Laboratory, and the present paper deals with waves corresponding to the reversible deposition of an insoluble substance.

Equations for the Complete Wave and the Peak Current

Boundary and Initial Conditions.—Consider the reduction of a substance Ox to another substance Red which is insoluble in the solution containing substance Ox or in the electrode material. If electrochemical equilibrium is assumed to be achieved at the electrode, it is permissible to apply the Nernst equation in order to correlate the activities of the substances Ox and Red. In order to simplify the calculations it is convenient to consider the case in which the activity of substance Red is assumed to be equal to unity. It can reasonably be expected that this hypothesis is verified when the electrode surface is coated with at least a monolayer of substance Red. When writing the Nernst equation it should be recalled that, in oscillographic polarography, the electrode potential E is a linear function of time of the form

$$E = E_i - vt \qquad (1)$$

In equation (1) E_i is the initial potential and v the rate of potential change. The second term $-vt$ on the right-hand of (1) is negative in the case of a cathodic process and positive for an anodic process, the European convention of electrode signs being used.

By taking equation (1) into account, the Nernst equation can be written under the form

$$(C_{ox})_{x=0} = \exp\left[\frac{nF}{RT}(E_i - E^0) - \ln f_{ox}\right]\exp\left[-\frac{nF}{RT}vt\right] \qquad (2)$$

where the subscript $x = 0$ indicates that C_{ox} is taken at the electrode surface; E^0 is the standard potential for the electrode process; f_{ox} the activity coefficient of the substance reacting at the electrode; and the other notations are conventional.

The initial potential E_i of the potential sweep should be such that virtually no current flows through the cell before the wave is recorded. Con-

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[1] J. E. B. Randles, *Trans. Faraday Soc.*, **44**, 327 (1948).

[2] A. Sevcik, *Collection Czechoslov. Chem. Communs.*, **13**, 349 (1948).