If independent values of the activity of Si were available, the equilibrium constant would fix the free energy of SiO_2. An effort was made by Chipman and co-workers[5] to fix this activity by distribution measurements between Fe and Ag. The experiments were done at 1420° at which temperature the lower limit of the liquid field has a mole fraction $N_{Si} = 0.14$. The equilibrium measurements were made at higher temperatures and lower concentrations. Extrapolation of the activity coefficient data could be made to agree with the free energy change in reaction (2) only by neglecting the distribution results at the lowest concentrations and adopting an unsatisfactory relation between $\log \gamma_{Si}$ and N_{Si}. The accepted value of ΔF^0 for SiO_2 led to $\log \gamma_{Si} = -2.14$ at 1873° K. and infinite dilution. A more satisfactory extrapolation of the distribution data gives $\log \gamma_{Si} = -3.4$ at 1420°, which is corrected by means of the known[5] partial molal enthalpy of Si (-28.5 kcal.) to give $\log \gamma_{Si} = -3.0$ at 1873° K. More recently Matoba, Gunji and Kuwana[8] have made direct measurements on reaction (2), at low concentrations of Si. Their data with the above activity coefficient give a free energy of formation of -138.5 kcal. at 1873° K. An uncertainty of ± 2 kcal. is inherent in the activity coefficient. This is to be compared with -130.0 kcal. in the tables.

III.—The activity of SiO_2 in metallurgical slags such as $CaO-SiO_2-Al_2O_3$ solutions at 1500–1700° has been studied by a number of investigators with grossly discrepant results. The four published experimental studies cover somewhat different ranges of concentration, but these overlap sufficiently in the binary system $CaO-SiO_2$ to permit comparison at $N_{SiO_2} = 0.45$. Fulton and Chipman[9] determined equilibrium concentrations at 1600° in the reaction

$$SiO_2(\text{in slag}) + 2C(\text{graphite}) = Si(\text{in Fe}) + 2CO(1 \text{ atm.}) \quad (3)$$
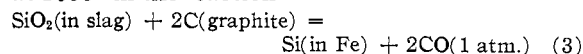
They used the activity coefficient of Si in the molten alloy which had been determined[5] and the accepted free energies of SiO_2 and CO to calculate a_{SiO_2}. Their value at $N_{SiO_2} = 0.45$ was 0.040. Baird and Taylor[2] and more recently Kay and Taylor[1] applied reaction (1) to slags and reported results at 1550° from which the interpolated activities of SiO_2 at $N_{SiO_2} = 0.45$ were 0.16 and 0.14, respectively. Yang, McCabe and Miller[10] used effusion measurements to obtain the activity of silica at 1637°. Interpolation to $N_{SiO_2} = 0.45$ gives $a_{SiO_2} = 0.28$. The direct measurements of the activity of SiO_2 are seen to yield values which are four to seven times as large as those obtained through reaction (3) and the accepted free energy of SiO_2. A four-fold correction in the equilibrium constant of this reaction would raise the activity coefficient by a factor of 4 and would require an adjustment of -5 kcal. in the free energy of formation of SiO_2.

(8) S. Matoba, K. Gunji and T. Kuwana, *Tetsu to Haganê*, **45**, 229 (1959); *Stahl und Eisen*, **80**, 299 (1960).

(9) J. C. Fulton and J. Chipman, *Trans. Am. Inst. Min. Met. Pet. Engrs.*, **200**, 1136 (1954).

(10) L. Yang, C. L. McCabe and R. Miller, "The Physical Chemistry of Steelmaking," John Wiley and Sons, Inc., New York, N. Y., 1958, p. 63.

IV.—Professor Wagner, in a private communication, has pointed out that the chemical potential of SiO_2 in a slag mutually saturated with Ca_2SiO_4 and $CaSiO_3$ may be calculated from the free energies of these compounds. The value so calculated confirms the results of Taylor and co-workers and is about 5 kcal. less negative than that interpolated from reaction (3) and the "third-law" free energy of SiO_2.

Research is in progress which is aimed at securing more accurate data on the several equilibria mentioned. Present accuracy is in all cases better than that corresponding to a discrepancy of 5 kcal. It is not easy to understand so large an error in the heat of formation or in the entropy of SiO_2, the latter amounting to $R \ln 4$. There are apparently no reasons for suspecting a zero-point entropy on structural grounds. On the other hand, the third-law value of ΔF^0 in reaction (1) is independent of the heat of formation of SiO_2 since that value is used in obtaining the heat of formation of SiC. Thus the discrepancy in this case could be either in the entropy of SiO_2 or in an equal error in two independent heats of combustion.

The fact that crystalline silicates require the same correction is readily understandable if the error is in ΔH. If, however, we have to add $R \ln 4$ to the entropy of SiO_2, it must be added not only for all the crystalline forms of silica but also for the silicates. Thus one cannot look for an entropy anomaly in the arrangements of SiO_4 tetrahedra but only within this structure. Clearly the problem requires theoretical attention as well as improved accuracy of measurement.

V. Addendum.—Since the foregoing considerations were initially set forth, the writer has seen an unpublished paper by Ramstad and Richardson[11] in which these equilibria were investigated

$$SiO_2(c) + H_2(g) = SiO(g) + H_2O(g) \quad (4)$$
$$Si(c) + SiO_2(c) = SiO(g) \quad (5)$$
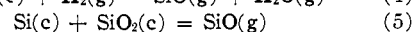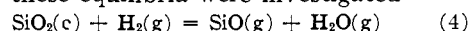
Combination of the results with the known free energy of formation of H_2O gave the free energy of formation of SiO_2. This was more negative by 3.8 ± 2 kcal. at 1700° K. than the third-law values listed in Coughlin's tables.[3]

(11) H. F. Ramstad and F. D. Richardson, "Silicon Monoxide," Feb., 1961, meeting, The Metallurgical Society of AIME.

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CONCERNING THE STABILITY OF SOME SUBSTITUTED CYCLOPROPENYL RADICALS; EVIDENCE FROM POLAROGRAPHY OF THE CORRESPONDING CATIONS

Sir:

The high stability of derivatives of the two-pi-electron cyclopropenyl cation[1] and the instability of a derivative of the four-pi-electron cyclopropenyl anion[2] are evidence for the "magic number" effect predicted by molecular orbital theory for such systems[3]; the same theory predicts that cyclo-

(1) R. Breslow and H. Höver, *J. Am. Chem. Soc.*, **82**, 2644 (1960). and references therein.

(2) R. Breslow and M. Battiste, *Chem. and Ind.*, 1143 (1958).

(3) *Cf.* S. L. Manatt and J. D. Roberts, *J. Org. Chem.*, **24**, 1336 (1959).

propenyl radicals, e.g., (II), should have less resonance stabilization than the corresponding cations. The only evidence on this point to date is the observation[4] that (III), the dimer of (II), does not dissociate, but models show that (III) is relatively unhindered while steric repulsion in the dimer is a major factor in many dissociations to free radicals.[5] Accordingly it seemed necessary to seek other evidence on the stability of the three-pi-electron cyclic conjugated system.

We have determined the polarographic reduction potential of the triphenylcyclopropenyl cation and compared it with that of the triphenylmethyl cation (IV). Since the two compounds are of similar size and shape it is expected that the difference in reduction potentials will result chiefly from the loss of resonance energy when (Ia) is transformed to (II). Simple m.o. theory predicts that the reduction of (IV) results in no loss of resonance energy, although this is of course an approximation and our comparisons really indicate only the difference between the ΔD.E. for reduction of (Ia) and that for reduction of (IV). Other correlations between polarographic reduction potentials and calculated changes in delocalization energy have been found by a number of authors.[6]

Ia, R = R' = R'' = H
b, R = R' = H, R'' = OCH₃
c, R = R' = R'' = OCH₃

III   IV
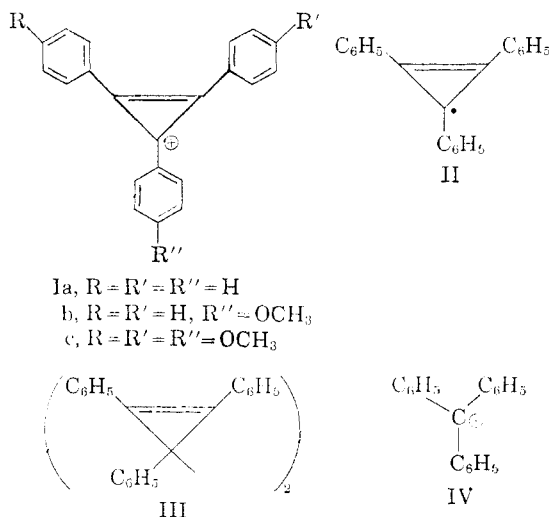
Since examination by d.c. polarography revealed that a reversible potential could not be obtained for (Ia) because of a rapid dimerization of the product (II), the technique of triangular wave potential oscillopolarography[7,8] was employed. Solutions 0.2 mM. in the cation perchlorates[9] were prepared in dry acetonitrile containing 0.1 M tetraethylammonium perchlorate, and the reference electrode was a silver wire in 0.1 M silver perchlorate in acetonitrile.[10] When (Ia) was examined at 10 c.p.s., only a cathodic wave was ob-

(4) R. Breslow and P. Gal, J. Am. Chem. Soc., 81, 4747 (1959).

(5) G. H. Wasserman in M. Newman, "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, p. 387.

(6) For reviews, cf. G. Holjtink, Chem. Weekblad, 56, 54 (1960); R. Daudel, R. Lefebvre and C. Moser, "Quantum Chemistry," Interscience Publishers, Inc., New York, N. Y., 1959, p. 276.

(7) J. Loveland and P. Elving, Chem. Revs., 51, 67 (1952).

(8) D. Smith and W. Reinmuth, unpublished work.

(9) All new compounds were fully characterized and their ionized state in solution was confirmed by ultraviolet spectroscopy.

(10) The potential of this reference electrode vs. the saturated calomel electrode is +0.380.

served, because of irreversible dimerization of the product radical, but at 150 c.p.s. the anodic and cathodic peak currents are equal, indicating that the radical can be reoxidized completely before dimerization. Using this technique the reversible reduction potential for (Ia) can be estimated as -1.132 ± 0.01 v., while that for (IV) is only -0.090 v. For (Ia) the dimerization is so rapid that d.c. polarography gives a value of -0.88 v., but in the case of (IV) the two methods agree, and high frequency oscillating potentials need not be employed to obtain the reduction potential uncomplicated by chemical kinetic processes. Using oscillopolarography we have also determined the reversible reduction potential of p-anisyldiphenyl cyclopropenyl cation (Ib) to be -1.24 v., while that of the corresponding trianisyl cation (Ic) is -1.49 v. Controlled potential coulometry of (Ia), (Ib), and (Ic) demonstrates that their reductions involve one electron, and the product from the reduction of (Ia) has been identified as (III). Analysis of the d.c. polarographic wave for (IV) indicates it undergoes a one-electron reduction.

It is obviously much more difficult to reduce the cyclopropenyl cations than it is to reduce the triphenylmethyl cation; if this difference is chiefly because of the loss of resonance energy resulting when the cyclopropenyl cations are converted to radicals, this corresponds to a loss of 1.04 e.v., or 24 kcal./mole, for (Ia) and of even more for the anisyl derivatives. This result roughly corresponds to the predictions of simple m.o. theory, in which ΔD.E.$_{red.}$ for (Ia) is predicted to be -0.504β while that for (IV) is predicted to be zero; the value of β appropriate to such changes has been suggested to be of the order of -2 e.v.[11] However, the agreement with simple m.o. calculations is by no means perfect, since from symmetry considerations it is predicted that the ΔD.E. for (Ib) should be precisely the same as that for (Ia); to accommodate the observed difference in reduction potentials, electron correlation must be considered.[11] The details of the relationship between m.o. calculations and observed reduction potentials in this series will be discussed in the full publication.

(11) A. Streitwieser, J. Am. Chem. Soc., 82, 4123 (1960).

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      RECEIVED FEBRUARY 25, 1961

ANTIPARASITIC DRUGS. IV. 2-(4'-THIAZOLYL)-BENZIMIDAZOLE, A NEW ANTHELMINTIC

Sir:

We wish to report the discovery of a new class of anthelmintic agents possessing a broad spectrum of activity for gastrointestinal parasites of domestic animals. Some of the compounds are among the most potent chemotherapeutic agents known, complete larvacidal activity being manifest in vitro at 10^{-5} γ/ml.[1] This potency coupled with the absence of activity toward other microorganisms and negligible mammalian toxicity

(1) Phenothiazine under similar conditions is active at about 10^{-1} γ/ml. Penicillin against a sensitive staphylococcus has an end-point of about 3×10^{-3} γ/ml. Cf. H. Welch, "Antibiotic Therapy," The Arundel Press, Inc., Washington, D. C., 1951, p. 62.