

With very dilute solutions at room temperature, three sharp breaks occur in the conductivity curve for the neutralization of Na_2SiO_3 with hydrochloric acid, suggesting the presence of ions from $\text{Na}_4\text{Si}_3\text{O}_8$, NaHSiO_3 at the termination of the respective stages. Titration of silicic acid freshly liberated from Na_2SiO_3 with sodium hydroxide at room temperature gave only two breaks. The first corresponded to $2\text{Na}_2\text{O} \cdot 3\text{SiO}_2$, the second to $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$.

When the measurements were made at the boiling point of water, the form of both curves changed considerably. Sodium silicate showed $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$ and $\text{Na}_2\text{O} \cdot 4\text{SiO}_2$, while boiling very dilute silicic acid showed only evidence of $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$.

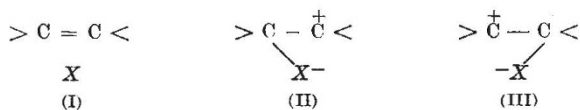
The observations were made with a Wien A.C. bridge, and the breaks in the conductivity curves increased in sharpness as the dilution increased. The solutions of sodium silicate were made immediately in cold water from Merck's Natrium silicium purum cryst. in $N/2$ solution in water, which analysis showed was $(\text{Na}_2\text{O} \cdot \text{SiO}_2)$ with water of crystallization.

F. H. CONSTABLE
S. TEGUL

Institute of Physical Chemistry,
University of Istanbul.

Co-ordinate Bond Formation by Olefins

IT is pertinent to add to Dr. Walsh's remarks¹ concerning co-ordinate bond formation by ethylene analogous to that commonly associated with formally saturated molecules possessing lone electron pairs that an essentially similar point of view was first presented by Winstein and Lucas². These authors visualized the olefin-electron acceptor (X) complex as a resonance hybrid involving the structures I, II and III:



and recognized the significance of this bonding to a wide range of olefinic reactivity. I pointed out the application of this concept to the aromatic hydrocarbon-poly-nitro compound addition complexes, using simple olefin complexes such as Reise's salt as illustration, at a meeting of the Chemical Society on October 15, 1942³, being at that time particularly interested in the rather remarkable rubber-silver nitrate compound⁴, which is another evident example of this structural type.

Similar association between donor and acceptor components has been envisaged by Woodward⁵ as the initial step in the Diels-Alder reaction. Pitzer⁶ has re-stated the basis of the Winstein-Lucas theory more precisely. Dewar⁷ has adduced evidence that donor acceptor complexes condition many rearrangements in aromatic systems, and has emphasized particularly the mobility of the bound quasi-cation over the whole electron cloud of the aromatic nucleus, thus permitting the electrophilic power of the ion to operate at the most favoured carbon centre.

Even quantitative data exist to supplement that provided by ionization potentials as cited by Walsh. Winstein and Lucas measured the heats of complex formation of methylethylethylene and cyclohexene with silver nitrate in aqueous solution, and found them to be nearly half that for the analogous silver ion complex with two molecules of ammonia; and Baughan, Evans and Polanyi⁸ have deduced that the

proton affinity of ethylene (174 kcal./gm. mol.) is only 10 kcal./gm. mol. less than that of water.

While I now concur with Walsh's preference for a simpler representation of this bonding than a multiple set of canonical structures, this issue is superficial—any symbolism of this kind is, to quote from Ingold, purely intellectual scaffolding.

L. BATEMAN

British Rubber Producers'
Research Association,
48 Tewin Road,
Welwyn Garden City,
Herts.

¹ Walsh, *Nature*, **159**, 165 (1947). Cf. also *J. Chem. Soc.*, 89 (1947).

² Winstein and Lucas, *J. Amer. Chem. Soc.*, **60**, 836 (1938). Cf. Taufen; Murray and Cleveland, *J. Amer. Chem. Soc.*, **63**, 3500 (1941).

³ A condensed report is given in *Chem. and Ind.*, **61**, 453 (1942).

⁴ Mark and Posnansky, *Rubber Chem. Tech.*, **13**, 519 (1940).

⁵ Woodward, *J. Amer. Chem. Soc.*, **64**, 3058 (1942).

⁶ Pitzer, *J. Amer. Chem. Soc.*, **67**, 1126 (1945).

⁷ Dewar, *J. Chem. Soc.*, **406**, 777 (1946).

⁸ Baughan, Evans and Polanyi, *Trans. Farad. Soc.*, **37**, 377 (1941).

Reduction of Potassium Permanganate in the Presence of Glass

AN interesting phenomenon has been recorded during an investigation in which the test for decomposable organic matter, by the determination of the amount of oxygen absorbed by $N/80$ potassium permanganate acidified by 25 per cent (v/v.) sulphuric acid, was employed and of which no previous record can be found.

During the preliminary stages of work on the breakdown of organic matter in lake waters, it was found that a significantly larger amount of oxygen was absorbed from acidified potassium permanganate by distilled water in the presence of small glass balls (3-4 mm. diameter) in comparison with the blank in the absence of glass balls. As this effect was likely to interfere seriously with future experiments involving the amount of oxygen absorbed from acidified potassium permanganate by various lake waters, it was necessary to study the effect in some detail; the results have proved to be of considerable interest and are summarized below. The official standard method for oxygen absorbed from potassium permanganate¹ was used throughout, except that in different experiments the period of incubation varied from 4 to 24 hours. Distilled water (100 ml.) from a metal still was used, and in all except the preliminary experiments it was collected in an aluminium container and used at once.

(1) Oxygen is absorbed by distilled water from acid permanganate in the presence of glass balls, crushed plate, bottle and 'Pyrex' glass, and silica (crushed 'Vitrosil'). With similar quantities (100 gm.) of the different types of glass and silica, crushed to approximately the same size-range, and dried and tested under identical conditions, there was no significant difference in the amount of oxygen absorbed by the different materials in view of the possible differences in surface areas involved:

'Pyrex'	Bottle	Plate	Silica
0.74	0.67	0.87	0.63 p.p.m.

(2) With small (3-4 mm.) or larger (10 mm.) glass balls and 'Pyrex' glass, the amount of oxygen absorbed was directly related to the weight of balls used.

Weight of balls	100 gm.	200 gm.	300 gm.
Oxygen absorbed (p.p.m.)	0.50	1.01	1.54
Weight of 'Pyrex' glass	108 gm.	140 gm.	
Oxygen absorbed (p.p.m.)	0.60	0.78	