

### Ionization Potentials of Carbonyl Molecules

THE first ionization energies of carbonyl molecules are largely determined by the non-bonding electrons at the oxygen atom of the carbonyl group. If electric charge flows from the other part of the molecule into the oxygen, the effective electro-negativity of that atom will become decreased, and hence the ionization potential of the molecule will be reduced<sup>1</sup>. From this point of view, it is expected that the magnitude of the ionization potential will serve as a clue to the state of electron transmission in a carbonyl molecule.

In the present work, measurements were made of the first ionization potentials by use of a Hagstrum type mass-spectrometer<sup>2</sup>. The evaluation of the potentials was made according to the critical slope method<sup>3</sup>, argon being employed as the calibration gas. The results are recorded in Table 1.

Table 1. FIRST IONIZATION POTENTIALS (eV.)

10.88 $\Delta = 0$	10.26 $\Delta = -0.62$	* $\Delta = ?$	11.51 $\Delta = 0.63$
10.26 $\Delta = 0$	9.89 $\Delta = -0.37$	10.36 $\Delta = 0.10$	10.66 $\Delta = 0.40$
9.74 $\Delta = -0.52$	10.21 $\Delta = -0.05$	10.51 $\Delta = 0.25$	

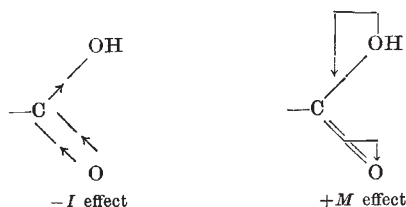
\* No measurement was possible on account of the scarcity of molecular ion formed.

It will be seen that the replacement of a hydrogen atom in  $\text{H}\cdot\text{CHO}$  and  $\text{H}\cdot\text{COCH}_3$  by  $\text{CH}_3$  or  $\text{CH}_2\cdot\text{CH}_3$  lowers the potential values, while replacement by  $\text{NH}_2$ ,  $\text{OH}$  or  $\text{OCH}_3$  tends to raise them. This trend in the potentials may be accounted for if the inductive mechanism is taken into consideration. That is, the Ingold's sequence<sup>4</sup> of  $-I$  effect is:

(a)  $\text{OH} > \text{NH}_2 > \text{H}$ ;  $\text{OCH}_3 > \text{NHCH}_3 > \text{H}$   
and that of the  $+I$  effect is

(b)  $\text{CH}_2(\text{CH}_3) > \text{CH}_3 > \text{H}$

This is rather surprising, since the mesomeric effect of the group (a) which counteracts the  $-I$  effect is supposed to be more important. Both effects are illustrated for the group  $-\text{CO}\cdot\text{OH}$ .



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K. HIGASI  
I. OMURA  
H. BABA

Research Institute of Applied Electricity,  
Hokkaido University,  
Sapporo, Japan.  
April 4.

<sup>1</sup> Coulson, C. A., "Valence", 186 (Oxford, 1952).

<sup>2</sup> Omura, I., Higasi, K., and Baba, H., *Bull. Chem. Soc. Japan* (in the press).

<sup>3</sup> Honig, R. E., *J. Chem. Phys.*, **16**, 105 (1948).

<sup>4</sup> Ingold, C. K., "Structure and Mechanism in Organic Chemistry", 71 (Ithaca, 1953).

### Effects of Pressure on the Superconducting Transition in Tin

RECENTLY, Muench<sup>1</sup> has investigated the displacement of the critical temperatures  $T_c$  of tin and indium produced by pressures of up to 100 atmospheres (obtained by compressing helium gas), and by a pressure of 1,900 atmospheres (obtained by the ice-expansion bomb technique); and he has measured the value of  $(\Delta H_c/\Delta p)_T$ , where  $H_c$  denotes the critical magnetic field and  $p$  the pressure, at temperatures between  $1^\circ\text{K}$ . and  $T_c$  for each of these metals. These experiments are important in that they provide the most complete data yet obtained on the effects of pressure on the superconducting transition.

In analysing his results, however, Muench assumed that  $(\partial H_c/\partial p)_T$  is independent of pressure. There is no satisfactory experimental evidence in support of this hypothesis: the earlier work of Kan, Sudovstov and Lasarew<sup>2</sup> at pressures of 1,350 and 1,700 atmospheres was not sufficiently accurate to allow one to deduce that  $\partial^2 H_c/\partial p^2$  is negligibly small, while Muench's own work only suffices to show that, at a given temperature,  $H_c$  is a linear function of pressure within experimental error over the very restricted range between 0 and 100 atmospheres. Indeed, a review of experimental results concerning second-order partial derivatives shows that the evidence in favour of  $(\partial H_c/\partial p)_T$  being substantially independent of pressure is much less convincing than is that in favour of  $(\partial T_c/\partial p)_H$  being substantially independent of pressure. Chester and Jones<sup>3</sup>, for example, have succeeded in extending almost tenfold the pressure-range over which the superconducting transition in tin has been observed without thereby being able to detect lack of linearity in the relationship between  $T_c$  and  $p$ ; and, although their accuracy was not of a high order at a pressure of 17,500 atmospheres, it is significant that, within experimental error, these results conform to the same straight line as do the less extensive measurements of Kan, Sudovstov and Lasarew.

By making use of a consistency relation between the first- and second-order partial derivatives which holds at any typical point on the  $H_c-T-p$  surface separating the superconducting and the normal phases, it is possible to devise an iterative computational procedure whereby the Muench assumption of pressure-independence of  $(\partial H_c/\partial p)_T$  can be dispensed with, and values for  $\partial^2 H_c/\partial p^2$  can be deduced from his data. Preliminary calculations made on this basis for the case of tin show that  $\partial^2 H_c/\partial p^2 = -8 \times 10^{-20}$  gauss dyne<sup>-2</sup> cm.<sup>4</sup> at the zero-pressure critical temperature of  $3.73^\circ\text{K}$ . The value of  $\partial^2 H_c/\partial p^2$  increases as the temperature is reduced, becomes zero at about