Ionization Potentials of Some Organic Molecules. IV. Troponoid Compounds

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A considerable amount of knowledge has been accumulated concerning the physical properties of troponoid compounds. Dipole moments, electron diffraction, X-ray analysis on crystals, near-ultra violet absorption, infrared absorption, Raman effect, magnetic susceptibilities, molecular refraction and the heats of formation have been investigated. Broadly speaking these results have been found to lead to consistent conclusions[1,2].

The object of the present paper is to supply ionization potential data of some troponoid compounds. As is well-known, the energy required to remove one of the most loosely bound electrons is given by

1) P. L. Pauson, *Chem. Revs.*, **55**, 9 (1955); T. Nozoe, "Progr. Chem. Org. Nat. Prod," Bd. XIII, Springer-Verlag, Wien (1956), p. 232.

2) For a review of these studies in Japan, see M. Kubo, Y. Kurita and M. Kimura, *Monogr. Res. Inst. Appl. Elec.*, **4**, 1 (1954).

the first ionization potential of the molecule. From this energy value, an important clue is obtained to the electronic state of a molecule.

Experimental Materials

Tropolone[1]: m. p. 50–51°C.

Tropone[1]: b. p. 84–85°C/6 mmHg, d_4^{25} 1.0825, n_D^{27} 1.6020.

2-Aminotropone[1]: m. p. 106–107°C.

Cyclohexanone:—this substance was kindly provided by Professor K. Kozima, Tokyo Institute of Technology—b. p. 52°C/24 mmHg.

Experimental Method and Result

The measurements of first appearance potentials were carried out in a Hagstrum type mass-spectrometer which was constructed by the present writers[3]. Comparatively weak ion currents were observed when the troponoid compounds were treated. In order to overcome the difficulty arising from this, special attention was paid to the space-charge effects[4] in the ionization chamber and also to the sensibility of the detector of ions.

The determination of the appearance potentials has been made by a modified method of critical slope as in a previous work[3]. Besides this the linear extrapolation method was employed for the sake of comparison. Ionization efficiency curves for tropolone and tropone are shown in Fig. 1.

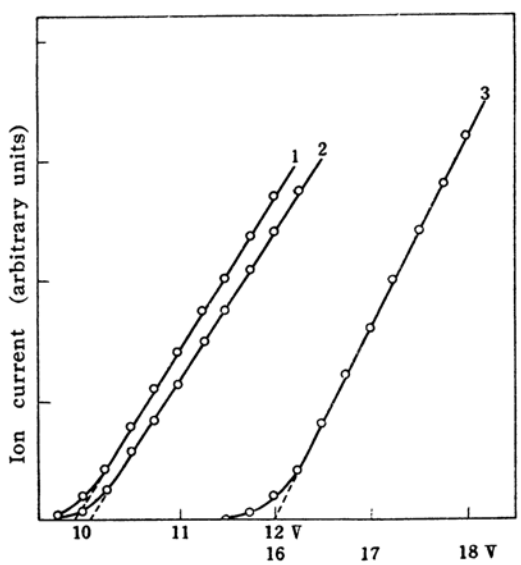

Fig. 1. Relative ionization efficiency curves for troponoids. 1 tropone; 2 tropolone; 3 argon.

The evaluation of the potential was made using the spectroscopic value for argon 15.76eV. Table I records the results thus obtained. No data for comparison exist in the literature.

TABLE I
FIRST IONIZATION POTENTIALS, eV.

Substance	Critical slope	Linear extrapolation
Tropone	9.68±0.02	9.69±0.02
Tropolone	9.86±0.02	9.83±0.02
2-Aminotropone	9.43±0.02	9.50±0.02
Cyclohexanone	9.91±0.05	9.83±0.05

Discussion

It has been concluded through the studies on dipole moment[5] and other properties[1] that the double bond of the carbonyl group

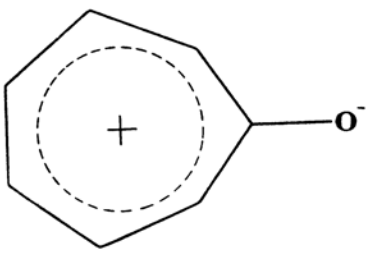

Fig. 2.

in tropone is exceptionally ionic, so that polar structure (Fig. 2) makes a large contribution to the normal state of the molecule. Concerning the structure of tropolone, it is believed that a strong hydrogen bond is formed between the two oxygen atoms of the molecule[1,5–7].

Are the above conclusions consistent with the observed ionization potentials? The answer will be affirmative, if this assumption be true: that, as in other carbonyl molecules[8–10] the first ionization energies of tropone and tropolone are largely determined by the nonbonding electrons at the O-atom of the carbonyl group.

Regarding tropone it is to be noted that both the critical slope and the linear extrapolation method gave lower ionization potential values than a related ketone, cyclohexanone by the amount 0.14–0.23 eV. The dipole moment of tropone 4.17 D[5] is

3) I. Omura, K. Higasi and H. Baba, This Bulletin, **29**, 501 (1955).
4) J. Marriott and J. D. Craggs, "Applied Mass Spectrometry," London (1954), p. 173.
5) Y. Kurita, S. Seto, T. Nozoe and M. Kubo, This Bulletin, **26**, 272 (1953).
6) K. Kuratani, M. Tsuboi and T. Simanouchi, ibid., **25**, 250 (1952).
7) S. Imanishi and M. Ito, ibid., **28**, 75 (1955).
8) C. A. Coulson, "Valence," Oxford (1952), p. 186
9) K. Higasi, I. Omura and H. Baba, *Nature*. **178**, 652 (1956).
10) I. Omura, K. Higasi and H. Baba, This Bulletin, **29**, 504 (1955).

the largest of the ketones, while cyclohexanone has a normal value of 2.75 D. Both of these facts may be interpreted as indicating that extra electric charge flows from the seven-membered ring into the oxygen. Consequently the effective electronegativity of the O-atom in tropone becomes smaller than in cyclohexanone, the ionization potential of tropone being thus decreased.

Further, by use of the same assumption the apparent rise in the potential of tropolone may be explained. Suppose that a strong hydrogen bond is formed between the two oxygen atoms in tropolone, that is, the non-bonding electrons of the oxygen atom of the carbonyl group become bound by the field of a proton. The energy for removing a loosely bound electron in tropolone will then become larger than in tropone.

The situation is more complicated in 2-aminotropone. It may be argued that only a weak hydrogen bond exists in the case of aminotropone[6]. Perhaps a decrease in ionization energy may result from this. But the observed decrease is more pronounced than is to be expected. It may be pointed out that the value 9.43 eV. for 2-aminotropone is near to that of methyl amine 9.41 eV. Generally aliphatic amines have lower potential values than corresponding ketones[10,11] e. g., ethyl amine 9.23 eV., *n*-propyl amine 9.17 eV., acetone 9.89 eV., methyl ethyl ketone 9.76 eV., etc. Therefore it may be reasonable to suppose that the most weakly bound electron in aminotropone is no longer situated at the O-atom. If it be localized at all, it will rather be near the N-atom of the NH_2 group.

Next, attention should be directed to the existence of pi-electrons in the seven-membered ring. Possibly these pi-electrons of the aromatic unsaturated carbon ring may be removed more easily than non-bonding electrons in the carbonyl group. But no reliable discussion can be presented on this possibility in the present stage of knowledge on this point.

Lastly a few words must be added concerning the difficulty of this sort of study. First, there are uncertainties in the interpretation of the ionization energy. For instance, against the explanation offered for tropone one may argue with good reason[8] that the measured ionization energy is very much higher than expected from the extremely ionic character of the carbonyl bond. Further one may point out that acetamide has a high ionization energy 10.39 eV.[10], so that the most loosely bound electron may not be localized at the N-atom of the molecule. In general it is questionable whether or not one can safely consider that the electron responsible for the first ionization is any one of the non-bonding electrons at a certain atom or that the ionization is due to pi-electrons of the conjugated system. Perhaps an *ad hoc* interpretation may be partly justified at the present stage, when few successful trials are known to explain the observed ionization potentials quantitatively even for the pi-electron systems containing no heteroatoms where molecular orbital calculations are relatively easy.

Second, some unknown source of error still exists in the measured potential values[12]. In the first report[3] of this series the writers tried to justify the use of argon as the standard gas and also the application of the critical slope method. The result of the examination was found satisfactory for eleven compounds. But one is not certain whether they are valid for any and every sort of molecule.

Summary

First ionization potentials are obtained for the four substances: tropolone (a) 9.86, (b) 9.83; tropone (a) 9.68, (b) 9.69; 2-aminotropone (a) 9.43, (b) 9.50; cyclohexanone (a) 9.91, (b) 9.83 (units being eV.). Classification symbols, (a) and (b), denote that the measurement was made either by the method of critical slope or by the linear extrpolation method. These results are consistent with the conclusions from other physical data under certain conditions.

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11) J. D. Morrison and A. J. D, Nicholson, *J. Chem. Phys.*, **20**, 1021 (1952).

12) See for instance, A. J. B. Robertson, "Mass Spectrometry," Methuen (1954), pp. 34-55. See also the subsequent paper of the writers.