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# METAL CHELATES OF HETEROCYCLIC NITROGEN-CONTAINING KETONES. XVII. EFFECT OF TEMPERATURE AND GAMMA IRRADIATION ON THE ELECTRICAL CONDUCTIVITY OF 2-QUINALDYL PHENYL KETONE AND ITS METAL COMPLEXES

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## ABSTRACT

The measurements of the electrical conductivity of 2-quinaldyl phenyl ketone, QPK, and its metal complexes were carried out in the temperature range 298–373 K. These compounds are found to possess semiconducting behaviour. The effect of gamma-irradiation on the electrical conductivity of these compounds in the $10^3$–$10^7$ rad range was studied. The conductivity of the complexes decreased on increasing the radiation dose and approaches that of the ligand. The increase in the activation energy, $\Delta E$ (eV), by radiation was found to be dependent on the crystal field stabilization energy in the case of a high spin tetrahedral field and the ionic potential of the metal ion.

## INTRODUCTION

It is well known that the semiconducting behaviour of the organic compounds, in a large number of cases, correlate with the energy difference between the highest occupied and the lowest empty $\pi$-molecular orbitals. This suggests that the transport of electrons in these systems involves the antibonding or nonbonding empty $\pi$-molecular orbitals of the compounds [1,2]. Gamma irradiation induces some changes in the chemical and physical properties of the organic compound as well as their complexes [3,4]. Among the effects produced is the degradation through the rupture of the metal-

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donating atoms bonds (oxygen, sulphur, nitrogen, etc.) in most of the metal complexes studied [3–5]. In a continuation of our previous studies of the factors affecting the electrical conductivity of the organic compounds and their metal complexes, we focus our attention onto the complexes derived from QPK. These complexes were studied and characterised in our laboratory, but their electrical conductivity is still obscure in the literature [6].

## EXPERIMENTAL

The preparation and characterization of QPK and the metal complexes of the title were reported previously [6]. The electrical conductivity of the samples was measured in the temperature range from 298 up to 373 K. The samples were prepared as tablets at pressures of 12 tonnes $\mathrm{cm}^{-2}$. The tablets were 10 mm in diameter and had a thickness of 0.3–0.5 mm. The samples were held between copper electrodes with silver paste in between and inserted, with the holder, vertically into a cylindrical electrical furnace. Both ends of the furnace were closed off to reduce drafts. The potential drop across the heater was varied gradually through a variac transformer to produce a slow rate of temperature rise to obtain accurate temperature measurements. The electrical measuring circuit consists of a regulated d.c. power supply Heathkit (0–400 V), Keithly multimeter for measuring current with sensitivity up to $10^{-9}$ amp. The temperature of the sample was measured to within $\pm 0.1$ K by means of copper–constantan thermocouple. The radiated samples were obtained by exposure to various absorbed doses up to $10^9$ rad using $^{60}$Co gamma 3500 NORTON in air at room temperature.

## RESULTS AND DISCUSSION

The variation of the electrical resistivity with temperature of the samples under investigation was obtained on cooling after raising the temperature up to 373 K. The electrical conductivity was calculated by using the general relation

$$\sigma = \frac{I}{V_c} \cdot \frac{d}{a}$$

where $I$ is the current in amperes and $V_c$ is the potential across the sample of cross sectional area $a$ $\mathrm{cm}^2$ and thickness of $d$ cm.

Selected data are represented in Fig. 1 and the data are summarized in Table 1. According to the data obtained, we could assume that these compounds possess semiconducting behaviour. This is clearly seen from the negative temperature coefficient of the electrical conductivity. The experi-

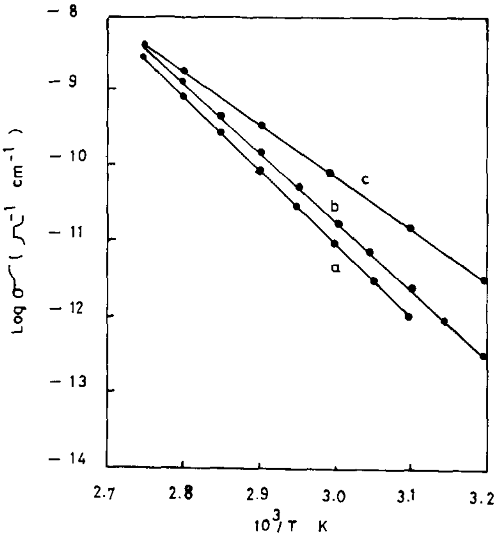

Fig. 1. Temperature dependence of electrical conductivity of: (a) QPK before irradiation; (b) $[Cu(QPK)_2]$ before irradiation; (c) $[Cu(QPK)_2]$ after irradiation ($10^7$ rad).

mental behaviour of the electrical conductivity of the selected compounds was found to fit well the well known equation

$$\sigma = \sigma_0 e^{-\Delta E/2KT}$$

where $\sigma$ and $\Delta E$ are the specific conductivity and the activation energy, respectively, $\sigma_0$ is the pre-exponential term, $K$ is the Boltzman's constant

TABLE 1

Effect of gamma irradiation on the electrical conductivity and the activation energy difference, $\Delta E$(eV), before and after irradiation of 2-quinaldyl phenyl ketone and its metal complexes

| Compound | Radiation dose (rads) | | | | |
|---|---|---|---|---|---|
| | $\sigma \times 10^{12}\ \Omega^{-1}\ cm^{-1}$ | | | | |
| | 0 | $10^3$ | $10^5$ | $10^7$ | $\Delta E$ |
| QPK | 1.02 | 1.02 | 1.02 | 1.01 | 0.71 |
| $[Sc(QPK)_3]$ | 2777.72 | 502.52 | 48.53 | 1.65 | 1.10 |
| $[Y(QPK)_3]$ | 2631.63 | 333.33 | 45.15 | 1.45 | 1.44 |
| $[La(QPK)_3]$ | 2083.34 | 259.77 | 35.54 | 1.46 | 2.80 |
| $[Mn(QPK)_2]$ | 1052.61 | 13.14 | 1.21 | 1.23 | 2.10 |
| $[Fe(QPK)_2]$ | 256.44 | 12.72 | 1.30 | 1.40 | 1.42 |
| $[Co(QPK)_2]$ | 161.08 | 13.07 | 1.37 | 1.45 | 0.64 |
| $[Ni(QPK)_2]$ | 165.53 | 13.69 | 1.34 | 1.37 | 1.12 |
| $[Cu(QPK)_2]$ | 190.44 | 10.47 | 1.10 | 1.11 | 2.20 |
| $[Zn(QPK)_2]$ | 163.93 | 10.64 | 1.20 | 1.24 | 0.98 |

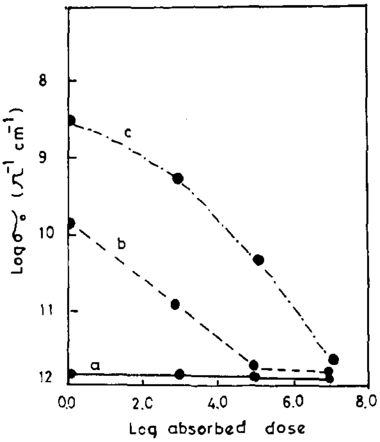

Fig. 2. The variation of log $\sigma_0$ with the absorbed gamma doses of: (a) QPK; (b) $[Sc(QPK)_3]$; (c) $[Co(QPK)_2]$.

and $T$ is the absolute temperature. Generally, with all ions, the electrical conductivity increases and the activation energy decreases in going from pure QPK to its metal complexes. This could be explained on the basis of the fact that the metal ions may act as a bridge facilitating the flow of the current [7]. The electrical conductivity of the investigated compounds was calculated for each gamma radiation dose and are tabulated in Table 1 and a representative curve is shown in Fig. 1. The data showed that the electrical conductivity of the trivalent metal complexes was found to be quite different from that of the divalent metal complexes. In the first case, the electrical conductivity decreased steadily with increasing the rad dose up to $10^5$ rad and then suddenly decreased up to $10^7$ rad. In the case of the divalent metal complexes, there is a small decrease in conductivity up to $10^5$ rad and again an increase to a maximum of $10^7$ rad. On the other hand, the conductivity of the ligand (QPK) is increased slightly with the radiation doses, Fig. 2.

During the thermal agitation, an additional increase of the electrical conductivity of the sample was observed. This predicts a certain discontinuity of the chemical bonds existing in the samples. This argument could be used as a useful criterion to ascertain the nature of the metal–ligand bonding. For copper (II) complex, for example, the following relation was derived

$$\Delta E = 0.0636 \log \sigma_0 + 1.74 \text{ eV}$$

The calculated results are given in Table 1. The variation of $\Delta E$ for the free ligand and its copper (II) complex with log $\sigma_0$ before and after γ-irradiation is shown in Fig. 3.

The decrease in the conductivity of the metal complexes which has a semiconducting behaviour with γ-irradiation has a significant effect in producing positive ions and electrons [8]. On prolonged irradiation many

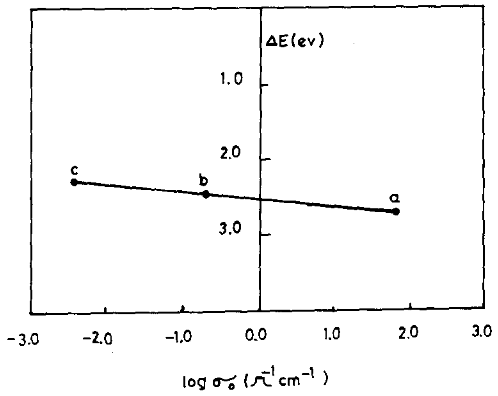

Fig. 3. Relationship between the activation energy change and log $\sigma_0$: (a) QPK before irradiation; (b) $[Cu(QPK)_2]$ before irradiation; (c) $[Cu(QPK)_2]$ after radiation ($10^7$ rad).

vacancies, interstitial anions and cations are created [9]. This defect may result in dissociation and/or recombination of the different anions and cations. This statement, together with the breakdown of the chemical bonds, in the complexes may be responsible for the decreased conductivity up to $10^5$ and $10^7$ rads for trivalent and divalent metal ion complexes, respectively. The increase of the electrical conductivity of the divalent metal ion complexes at high γ-irradiation doses could be attributed to the fact that the

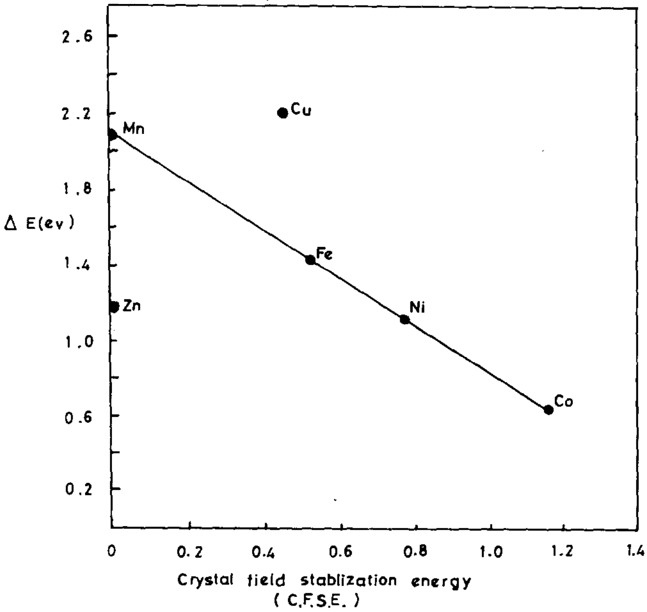

Fig. 4. Relationship between $\Delta E$(eV) and the C.F.S.E. of high spin tetrahedral field.

gamma absorbed doses may lead to a partial destruction along the chelate bond at the initial stage followed by cross-linking and/or creation of free radicals causing the observed increase in the electrical conductivity and the decrease in the corresponding activation energy [7–9] for conduction, Fig. 1. The calculated values of $\Delta E$ (eV), the difference between the activation energies before and after gamma irradiation, are given in Table 1. It is shown that there is an increase in the activation energy with radiation dose while the materials under investigation still possess their semiconducting behaviour. This could be explained on the basis of the mobile electron hypothesis [10,11], i.e., the $\pi$-electrons remained delocalized over the separated molecules produced from the gamma damage. The increase in the activation energy difference was found to be in the order $E_{M^{+3}} > E_{M^{+2}} > E_{\text{ligand}}$. This behaviour could be explained on the basis that the number of stakes of the quinaldine ring in the trivalent metal ion complexes is greater than that in the divalent metal ion complexes. The activation energy changes $\Delta E$ (eV) for the divalent metal ion complexes were found to be in the order Mn > Fe > Co < Ni < Cu > Zn which is the reverse of the order of the crystal field stabilization energies of these ions in high spin tetrahedral field environment as seen in Fig. 4. The complex of Zn(II) deviates from this sequence because it possesses different crystal field environments.

The dependence of the change in energy of activation on the ionic potential ($Z/r_0$ $\text{A}^{-1}$), Fig. 5, for the trivalent compounds was found to be in the order La > Y > Sc. This feature could be discussed on the basis that the higher the ionic potential, the lower the activation energy difference ($\Delta E$).

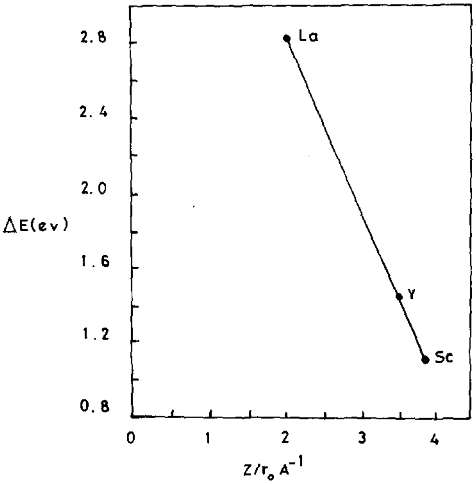

Fig. 5. Relationship between $\Delta E$(eV) and the ionic potential $Z/r_0$ ($\text{A}^{-1}$).

## REFERENCES

1 H. Kallmann and M. Silver, Symposium on Electrical Conductivity in Organic Solids, Interscience, New York, 1961, p. 137.
2 D.D. Eley, G.D. Perry and D.H. Taysum, Trans. Faraday Soc., 49 (1953) 79.
3 J.F. Kircher and R.E. Bowman, Effect of Radiation on Materials and Compounds, Reinhold, New York, 1964, p. 271.
4 H.F. Aly, F.M. Abdel Kerim and A. El-Agramy, Isotopenpraxis, 13 (1977) 50.
5 M.M. Abou-Sekkina, A. El-Dissouky and M.M. Osman, Thermochim. Acta, 55 (1982) 231.
6 A. El-Dissouky, S.A. El-Shazly and M. Gaafar, Transition Met. Chem., 8 (1983) 175.
7 P.S. Gomm, T.W. Thomas and A.E. Underhill, J. Chem. Soc. A, (1971) 2154.
8 Dugisbe R.D. Dugisbe, Report of Bristol Conference on Defects in Crystalline Solids, The Physical Society, London, 1955, p. 246.
9 R.G. Charlies, H. Freiser, R. Foriedel, I.E. Hillard and H.W. Johnson, Spectrochim. Acta, 15 (1956) 109.
10 J. Vinyard and J. Pienes, Radiation Effect in Solids, Mir, Moscow, 1960, p. 398.
11 S.J. Ashcroft, Inorganic Thermodynamics, Van Nostrand Reinhold, New York, 1973, p. 192.