Thermochimica Acta, 45 (1981) 209—212 209
Elsevier Scientific Publishing Company, Amsterdam — Printed in Belgium

Note

THE ENERGETICS OF CHARGE TRANSFER COMPLEXES OF AN ANTIOXIDANT WITH VITAMIN K DERIVATIVES

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(Received 7 October 1980)

The antioxidant *N*-phenyl-2-naphthylamine acts as a booby trap for biochemists because it is found as a contaminant of lipid extracts containing vitamin K and is the result of charge transfer (CT) complex formation between antioxidant and vitamin K derivatives [1]. Such complex formation is highly likely because phenolic and amine antioxidants in general possess comparatively low ionization potentials (7—9 eV) [2] and are therefore expected to function as powerful electron donors under favourable circumstances. Since quinone type structures are present in vitamin K, the spectroscopic studies on the CT complex formation between various quinones and the antioxidant *N*-phenyl-2-naphthylamine have been reported from time to time by various workers [3,4]. However, the energetics of these CT complexes have not been studied in detail and even where the experimental data on the energy parameters of these complexes are reported, they are not very reliable, as pointed out by Dwivedi and Rao themselves [4]. Therefore we considered it interesting to calculate theoretically the energy parameters of *N*-phenyl-2-naphthylamine with a few quinone acceptors in order to understand the magnitude of CT interaction responsible for the booby trap. The energy parameters have been computed employing the model of Sonnesa and Daisey [5] and the empirical relationship reported from our laboratory [6,7]. The calculated values of the energy parameters along with the experimental and predicted value of enthalpy of formation, ΔH, from the empirical relationship are given in Table 1.

It is quite evident from Table 1 that the value of interaction energy, G_0 depicted from the equation

$$G_0 = \Delta H - X_0$$

where X_0 is the resonance interaction energy of the ground state of the CT complex, follows the expected trend [7]. The agreement between the experimental and theoretical values of ΔH is not good (Table 1). The theoretical value of % charge transfer, F (Table 1) reveals that the strength of the CT complexes decreases in the order:

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TABLE 1

Experimental and theoretical energy parameters for the CT complexes of quinones with *N*-phenyl-2-napthylamine (in eV except *a*, *b* and *F*)

	$h\nu_{CT}$	Δ	$-X_0$	X_1	G_0	$-\Delta H$		a	b	F
						Obs. *	calc. †			
Group A acceptors										
1,4-Benzoquinone	2.480 *	0.33	1.03	1.12	0.73	0.04	0.30	0.70	0.65	46.9
Group B acceptors										
1,4-Napthaquinone	2.610 *	0.75	0.86	1.01	0.65	0.04	0.21	0.76	0.58	38.3
2,3-Dimethyl napthaquinone	2.683 **	0.92	0.80	0.96	0.61		0.14	0.78	0.55	34.9
2-Methyl napthaquinone	2.818 **	1.20	0.71	0.90	0.56		0.15	0.81	0.51	30.3
2,3-Dimethyl anthraquinone	2.850 *	1.26	0.70	0.89	0.55	0.16	0.15	0.82	0.50	29.4

* Ref. 4.

** Ref. 3.

† Predicted from the empirical formula.

$\beta_0 = -1.20$ eV, $S_{01} = 0.1$.

1,4-benzoquinone > 1,4-naphthaquinone > 2,3-dimethylnaphthaquinone >
2-methyl-naphthaquinone > 2,3-dimethylanthraquinone

Further, a comparison of the % charge transfer among 1,4-benzoquinone, 1,4-naphthaquinone and 2,3-dimethylanthraquinone shows that the decrease in % charge transfer with increase of per benzene ring is of the order of 9%. However, the trend based on the experimental value of ΔH reported by Dwivedi and Rao [4] is

2,3-dimethylanthraquinone > 1,4-naphthaquinone ≈ 1,4-benzoquinone

The difference between the theoretical values of ΔH computed by us and the experimental values [4] showing the reversibility in the trend of the stability of these CT complexes may be due to the following factors: (i) it is likely that the equilibrium constants reported by the earlier authors [3,4] are in error since the method of evaluation [8] of these quantities is very sensitive to [donor], and (ii) it is difficult to measure experimentally the energetics of CT complexes because of weak interaction between donor and acceptor and also due to the interaction of the solvent with donor and acceptor. Hence, we feel that the computed values of ΔH are more reliable than the experimental values reported by earlier workers [4].

Table 1 shows that there is small variation found for any one set of energy terms. This effect is apparently due to the small variations in the value of $h\nu_{CT}$ and ΔH among these complexes. There are, however, some variations observed as the strength of the complex measured by ΔH increases. With respect to these variations the complexes are classified into two groups: (A) the strong complexes; (B) the weak complexes formed from the respective acceptors (Table 1).

Further, if we compare the energy terms of these complexes (Table 1) some trends become apparent, e.g. n—σ [5,9,10] and n—π [7] type complexes. Table 1 reveals that the value of Δ is inversely proportional to the strength of the complexes and is in agreement with the findings of earlier workers [5,7,9,10]. The large positive value of G_0 gives rise to a smaller value of Δ. Since in weak complexes the electrostatic forces of attraction predominate, the value of G_0 becomes negative. The positive value of G_0 for the system considered here supports the earlier prediction that in stronger complexes with a short D—A distance the repulsive forces will predominate over the attractive forces. The increase in the negative value of X_0 in the ground state follows the trend of ΔH, i.e., X_0 is directly proportional to ΔH. This could perhaps best be explained by the fact that the increase in the contribution of resonance interaction, and hence charge transfer, is responsible for the stabilization of the ground state in these complexes.

The electrostatic terms in the case of weak complexes make significant contributions, and in most cases the electrostatic terms outweigh the charge transfer resonance contributions [11]. Since in stronger complexes the electrostatic terms are operative, the value of X_0 as well as the trend of these values for their CT complexes (Table 1) led us to conclude that the CT interaction makes a significant contribution to the stability of the ground state, like those of the n—σ and n—π types of complexes [5,7,9,10].

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