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IR SPECTRA OF THE CYCLOOCTATETRAENE DIANION PREPARED BY MATRIX REACTIONS WITH ALKALI METALS

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Summary

The IR absorption spectra of pure dipotassium and disodium salts of the cyclooctatetraene (COT) dianion formed by matrix reaction with alkali metals were measured. It is shown that the absorption band in the 1300 cm^{-1} region should be assigned to the ν(C—C) stretching vibration of the COT^{2-} dianion.

A dependence of the frequency of the out-of-plane bending ρ(C—H) vibration on the nature of the cation is established.

Of the numerous donor—acceptor interactions in chemical reactions those involving complete charge transfer are of particular interest. These interactions lead to formation of anion-radical or dianion systems. Naturally, the electronic structure of the interacting molecules undergoes changes leading, in certain cases, to alteration of the geometry of the acceptor. From this point of view it is interesting to study the cyclooctatetraene molecule. The eight-membered ring of this cyclopolyene, according to electron diffraction data [1,2], has a bath structure (D_{2d} symmetry) with alternating single and double bonds. Since the p_z orbitals of carbon atoms forming adjacent double bonds do not overlap, there is no conjugation and the molecule is a typical non-aromatic olefin [3,4]. On reduction with alkali metals cyclooctatetraene first attracts one electron, forming an anion-radical (COT$^{-\cdot}$) with the unshared electron delocalized along the perimeter of the molecule. ESR data [5] show that the anion-radical is characterized by a hyperfine structure suggesting interaction of the unshared electron with eight equivalent protons.

According to quantum-mechanical calculations [6], the anionic system is stabilized in the electron state that obeys the Hückel rule of aromaticity ($4n + 2$, $n = 2$) and therefore should tend to attract another electron to complete its ten π-electron aromatic system. Such processes do in fact take place: cyclooctatetraene reacts intensively with two gram-equivalents of metallic potassium in tetrahydrofuran solution forming a dipotassium salt of the dianion. The pure di-

TABLE 1

SELECTION RULES AND MAIN VIBRATIONS OF THE CYCLOOCTATETRAENE DIANION (D_{8h} symmetry)

Vibration	Number of vibrations	IR and Raman activity
A_{1g}	2	Raman
A_{1u}	—	inactive
A_{2g}	1	Raman
A_{2u}	1	IR
B_{1g}	2	inactive
B_{1u}	2	inactive
B_{2g}	2	inactive
B_{2u}	—	inactive
E_{1g}	1	Raman
E_{1u}	3	IR
E_{2g}	4	Raman
E_{2u}	2	inactive
E_{3g}	2	Raman
E_{3u}	4	inactive

anion salt has not yet been studied by X-rays *. However a study of a 1/1 adduct of the dipotassium salt of cyclooctatetraene with diglyme has recently been described [7]. It was shown that potassium cations are arranged on an 8-order axis above and below the cyclooctatetraene dianion plane. The plane is a planar equilateral octahedron with C—C lengths of 1.40 Å and C—C—C angles of ~135° (D_{8h} symmetry).

Two papers have been published by Fritz and Keller that report the IR absorption spectra of the tetrahydrofuranate of the dipotassium salt of the dianion ($K_2C_8H_8 \cdot THF$). In the first study [8] absorption bands were observed at 2994, 1715, 1669, 1531, 1424, 1292, 1137, 1057, 877, 805 and 681 cm^{-1}. In the following work [9] the authors reported additional IR data but the spectrum turned out to be more complex. The authors tentatively assigned the 681 cm^{-1} band to out-of-plane β(C—H) vibrations, 1715, 1669 and 1531 cm^{-1} bands to combinational tones and the band in the 1424 cm^{-1} region to skeletal stretching ν(C—C) vibrations. The spectrum obtained by Fritz and Keller is the only one published on the cyclooctatetraene dianion. It should be noted that they report a very complex spectral pattern, whereas theoretical analysis gives only four vibrations in the case of D_{8h} symmetry (Table 1).

In a survey by Fritz published in 1964 [10], the Table of IR absorption bands of the potassium cyclooctatetraene salt includes only four bands at 2994, 1431, 880 and 684 cm^{-1}, but it is not explained why these bands are assigned to the main vibrations of the cyclooctatetraene dianion. To our knowledge the spectra of pure cyclooctatetraene salts have not yet been studied.

We undertook the present investigation with the aim of recording the IR spectra of pure potassium and sodium salts of the cyclooctatetraene dianion.

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* It should be noted that crystals of the dipotassium dianion salt are very difficult to work with since they are very unstable and explode exposed to air.

We used the method of isolation of zerovalent atomic metal (potassium or sodium) in a cyclooctatetraene matrix at low temperature. A sample of the dianion salt is formed on a cryostat KBr support by interaction of the alkali metal with the cyclooctatetraene matrix. An advantage of this method is that synthesis of the salt is carried out directly in the cryostat cell adapted to measurement of IR and ESR spectra and the presence of solvents, moisture and oxygen is excluded since the processes are carried out under high vacuum (10^{-6} Torr). Cyclooctatetraene reduction may proceed by single- or two-electron reactions so we first studied the ESR spectra of samples obtained by co-condensation of atomic sodium or potassium with cyclooctatetraene on a glass support at low temperature. No resonance signals were observed indicating the absence of paramagnetic species in the samples. Strictly speaking this suggests either no chemical interaction between the metal and cyclooctatetraene or two-electron reduction of the latter with formation of a diamagnetic dianion. A parallel IR study of similar samples (described below) shows that the second alternative is in fact the case, i.e. in given conditions two-electron reduction of cyclooctatetraene takes place in non-solvating media.

Comparison with pure cyclooctatetraene (prepared by condensation on KBr support cooled to —185°C) shows that the IR spectra of cyclooctatetraene matrices of zerovalent alkali metals (sodium(0) or potassium(0)) (Fig. 1) reveal several new bands indicating chemical interaction, presumably, with formation of a dianion salt. The neutral cyclooctatetraene molecule has a D_{2d} symmetry and, in accordance with the corresponding selection rules, 15 IR vibrations are allowed: $5B_2 + 10E$. On formation of the aromatic system of the dianion the eight-membered ring becomes planar, the C—C bonds are levelled out and the new molecule acquires D_{8h} symmetry with four IR-active vibrations allowed ($3E_{1u}$ and A_{2u}). Indeed, four absorption bands at 700, 880, 1300 and 3000 cm^{-1} appear in the spectra of alkali metal matrices. These data agree with the results obtained by Fritz and Keller for the dipotassium salt of the cyclooctatetraene dianion.

Since the vapour pressure of cyclooctatetraene is sufficiently high whereas the salt is completely nonvolatile, we decided to remove the excess cyclooctatetraene by gradual heating under vacuum. This operation proved to be very effective and made it possible to entirely remove the unreacted cyclooctatetraene and to record the IR absorption spectra of the pure dipotassium and disodium

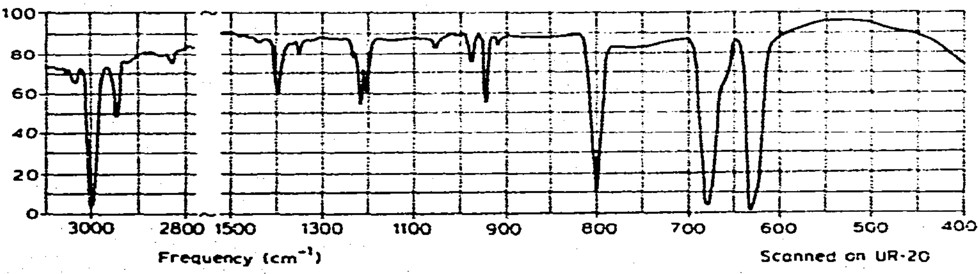

Fig. 1. IR absorption spectrum of pure cyclooctatetraene, T 93 K.

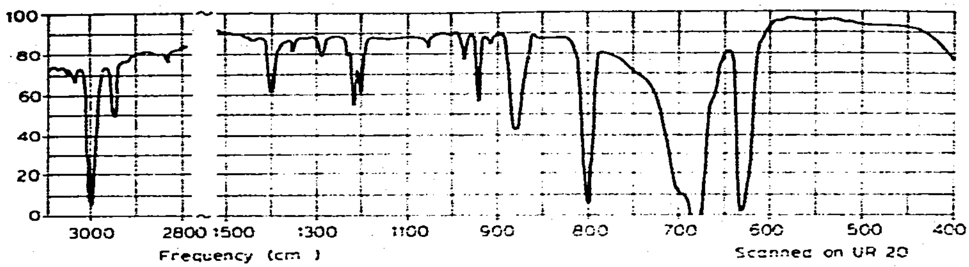

Fig. 2a. IR absorption spectrum of the cyclooctatetraene matrix of atomic zerovalent sodium *T* 93 K.

dianion salts (Fig. 2). The general pattern of the spectra and the complete agreement with the theoretically predicted pattern unequivocally shows that they belong to the dianion salts.

The absorption bands in both spectra (potassium and sodium salts) have similar frequencies. The only band that differs and has a considerably lower frequency in the case of the potassium salt is the 700 cm^{-1} band of bending ρ(C—H) vibrations.

The effect of the cation nature in alkali metal—cyclooctatetraene ionic pairs has been observed previously by other methods. Thus, a dependence of the chemical shifts of the ring protons on the nature of the cation was established in the PMR spectra of ether solutions of alkali metal salts of the cyclooctatetraene dianion [11].

Therefore, the results obtained in the present work extend the experimental observation of the cation effect in the alkali metal—cyclooctatetraene dianion ionic pair to vibrational spectra (out-of plane bending C—H vibrations).

The IR spectrum of K_2COT^{2-} is in good agreement with the data reported by Fritz and Keller, the only important exception being the absence of the 1430 cm^{-1} band that was assigned in ref. 10 to the main vibration of the cyclooctatetraene dianion. The absence of several other bands is explained by the fact that they are due, according to Fritz and Keller, to vibrations of the adduct of the dianion salt with tetrahydrofuran. We thought it possible that the 1430 cm^{-1} band is also not associated with the main dianion vibrations. To check this point, we recorded the IR spectrum after treating a sample of pure K_2^+

Fig. 2b. IR absorption spectrum of the pure disodium salt of the cyclooctatetraene dianion, *T* 93 K.

TABLE 2

ASSIGNMENT OF THE MAIN IR-ACTIVE VIBRATIONS OF THE CYCLOOCTATETRAENE DIANION

Vibration		Assignment according to Fritz and Keller [10]	Assignment according to our data	
		$K_2^+COT^{2-}$	$K_2^+COT^{2-}$	$Na_2^+COT^{2-}$
ν(C—H)	E_{1u}	2994	2995	3000
ν(C—C)	E_{1u}	1431	1295	1290
β(C—H)	E_{1u}	880	880	880
ρ(C—H)	A_{2u}	684	675	695

COT^{2-} on a cryostat support with dry air. An intensive absorption band appeared in the 1430 cm^{-1} region. Therefore, this band is due to an oxidation product of the dianion salt and should not be assigned to the main vibration of the dianion salt.

In the region of ν(C—C) stretching vibrations an absorption band at 1300 cm^{-1} is observed that is also present in the spectrum of K_2^+ COT^{2-} obtained by Fritz and Keller. In our opinion, the ν(C—C) stretching vibration of the cyclooctatetraene dianion should be assigned to this band and we propose a new assignment of the main IR-active dianion vibrations (Table 2).

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