

# Photoionization of Anions in Rigid Media: Absorption and Emission Spectroscopy of Cyclooctatetraene Radical Anion, Its Ion Pairs, and Triple Ions

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**Abstract:** Photoionization of salts of the cyclooctatetraene dianion ( $\text{COT}^{2-}$ ) with alkali metal cations ( $\text{M}^+$ ) in a 2-methyltetrahydrofuran glass at 77 K led to the formation of triple ions  $2\text{M}^+\text{COT}^-$ , which were further transformed into ion pairs  $\text{M}^+\text{COT}^-$  and free  $\text{COT}^-$  ions. Attempts to effect further ionization and to observe the so far hypothetical planar  $\text{COT}^-$  triplet were unsuccessful. Fluorescence from  $2\text{M}^+\text{COT}^{2-}$ ,  $2\text{K}^+\text{COT}^-$ ,  $2\text{Rb}^+\text{COT}^-$ , and  $2\text{Cs}^+\text{COT}^-$  was observed. In striking contrast,  $\text{COT}^-$ ,  $\text{M}^+\text{COT}^-$ ,  $2\text{Na}^+\text{COT}^-$  (and probably  $2\text{Li}^+\text{COT}^-$ ) do not emit. The absorption, emission, and ordinary as well as polarized excitation spectra indicate that  $\text{COT}^-$  is planar and fairly rigid in the ground and lowest excited doublet state, at least in form of some of its ion clusters, and that the counterions are located on a fourfold or eightfold symmetry axis.

Photoejection of electrons from anions in a rigid glass is a well-known phenomenon.<sup>2</sup> The anions have been shown to be converted to the parent hydrocarbons (double anions to monoanions), the ejected electrons are trapped in the glassy solvent, and their presence can be detected by near-infrared absorption and by ESR spectroscopy. The nature and generality of the phenomenon are presently well enough understood that it appears entirely feasible to exploit it for preparation of novel hydrocarbons and radical ions from electron-rich species. The latter are sometimes much more easily accessible, a classical example being the pentalene dianion which has been known for more than a decade, while pentalene radical anion is unknown, and pentalene itself appears to be extremely elusive.<sup>3</sup>

This approach to new hydrocarbons makes sense particularly in instances in which their expected reactivity is so high that conventional techniques fail and matrix-isolation studies followed by spectral techniques are called for. In such cases it is very useful to have several precursors available and an electron-rich ion might well be one of these. Reactivity studies may be possible after the glass is melted if the ejected electrons are first scavenged by a suitable trapping agent.

It is also worth noting that, at least in principle, in photoejection of an electron from a doublet ground state of a radical anion with light of suitable wavelength, spin selection rules permit not only the formation of a singlet but also of a triplet state of the neutral product. The possibility of opening a new pathway to triplet molecules provides an additional incentive for the present line of investigation.

Since some anions and many double anions will be present in the form of tight ion pairs or triple ions in glass-forming solvents such as 2-methyltetrahydrofuran,<sup>2,4</sup> photoejection will usually not lead to perturbation-free hydrocarbons or radical anions. This may be considered a disadvantage if preparation of the free species is the goal, but on the other hand, the availability of a choice of counterions permits an observation of the new species under a variety of minor perturbations and this can be very valuable, particularly in electronic spectroscopy, where a study of perturbation-induced shifts should often allow a differentiation of spectral features due to vibrational sublevels from those due to several independent electronic transitions. The effects of nearby positive charges on properties of neutral hydrocarbons might be of considerable interest in themselves in view of their possible relation to adsorption phenomena. Also, clusters of two positive ions with an anion carrying a single negative charge are not easily accessible otherwise.

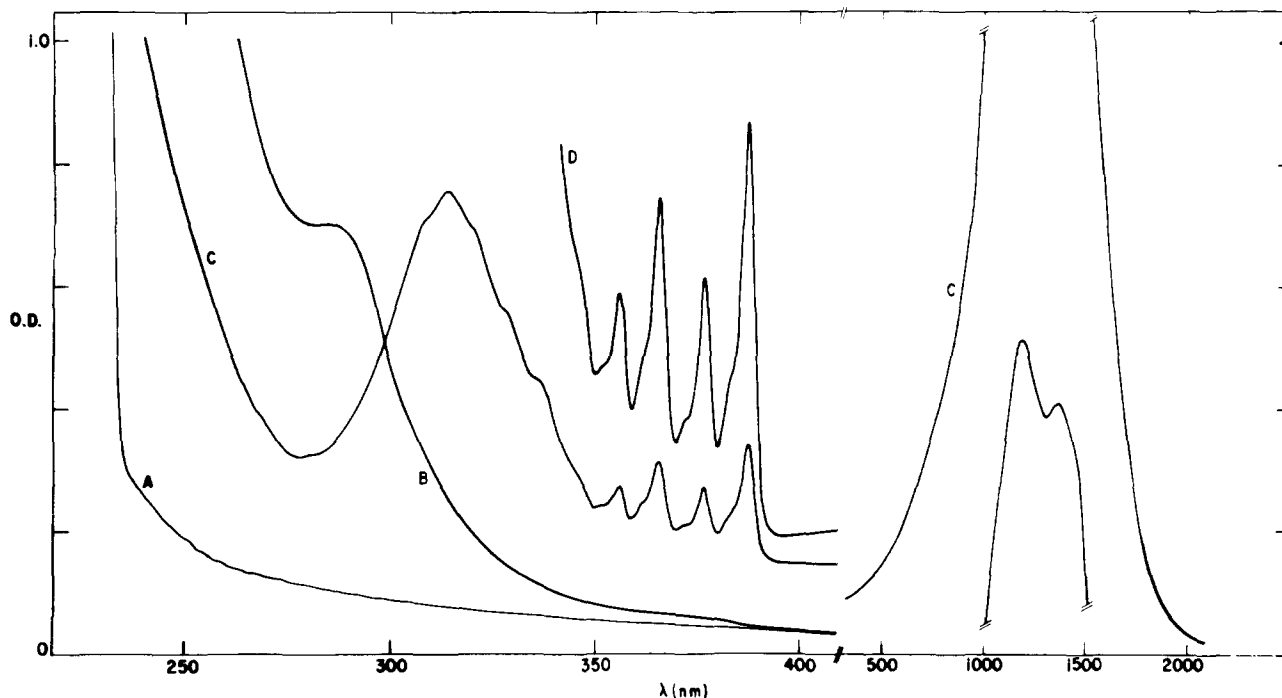
Before engaging in an investigation of novel hydrocarbons and ions,<sup>3b</sup> we have decided to reaffirm the generality and applicability of the method on a model system in which the product was known but its electronic spectrum had not been studied extensively. We have chosen the cyclooctatetraene dianion ( $\text{COT}^{2-}$ ), which is expected to give the radical anion ( $\text{COT}^-$ ) in the first step. The uv absorption spectrum of  $\text{COT}^-$  in liquid ammonia<sup>5</sup> and its ESR spectrum<sup>5-7</sup> have been published. While our work was in progress, the absorption curve in 2-methyltetrahydrofuran (2-MTHF) was also published,<sup>8</sup> as was a report that photoejection from  $\text{COT}^{2-}$  can be accomplished in fluid solutions and monitored by ESR spectroscopy.<sup>6</sup>

The choice of  $\text{COT}^{2-}$  for our first experiments was dictated by two additional considerations. First, it is important to find out how firmly bound the electrons can be before the photoejection fails to occur with photons for which glassy 2-MTHF is still transparent ( $\lambda > \text{ca. } 235 \text{ nm}$ ), since this ought to be perhaps the most serious limiting factor for the present version of the method. This photoejection threshold should be related to the energy of the highest occupied molecular orbital (HOMO) and should depend on the presence of counterions. In  $\text{COT}^{2-}$ , the HOMO is nonbonding, whereas it is antibonding in most of the hydrocarbon ions studied so far, so that  $\text{COT}^{2-}$  is a fairly difficult test case. Second, if it turned out that both electrons can be photoejected,  $\text{COT}$  itself should be formed. It seemed to us that there was a slight chance that  $\text{COT}$  might be formed in a vertical process as a planar octagonal triplet which, at that geometry, could represent the ground state and thus be metastable with respect to conversion to the ordinary nonplanar singlet. Such a species would be of considerable theoretical interest.

The present paper reports a preparation of  $\text{COT}^-$  in rigid 2-MTHF by photoejection from  $\text{COT}^{2-}$  and describes its absorption and ordinary and polarized fluorescence emission and excitation spectra in the presence of one or two alkali metal counterions. Attempts to prove the presence of planar triplet  $\text{COT}$  have given only ambiguous results.

## Experimental Section

Solutions of  $\text{COT}^{2-}$  salts in 2-MTHF were obtained by reaction of  $\text{COT}$  in 2-MTHF with metal mirrors or metal chunks (Li) using standard high-vacuum techniques. 2-MTHF (MCB chromatography reagent) was refluxed with Na-K alloy (MSA Research Corp.) for several hours, fractionally distilled through a 3-ft column, transferred into a vessel containing  $\text{LiAlH}_4$  or Na-K alloy, degassed, and distilled in vacuo into a storage bulb containing tetra-



**Figure 1.** Absorption spectra in 2-MTHF at 77 K (3-mm path length): (A) baseline for spectra B and C below 400 nm; (B)  $(1.5 \pm 0.3) \times 10^{-4}$  M  $2K^+COT^{2-}$ ; (C)  $2K^+COT^- + e^-(solv)$ , obtained from B by 254-nm irradiation ( $90 \pm 10\%$  conversion). The right-hand side of curve C (above 400 nm) has been corrected for baseline. The insert between 1000 and 1500 nm has been shifted down by 1.0 unit of O.D. (D) A more concentrated solution of  $2K^+COT^- + e^-(solv)$ , obtained by irradiation of ca.  $5 \times 10^{-4}$  M  $2K^+COT^{2-}$ .

cene and Na-K alloy. COT (BASF) was freshly vacuum-distilled just before use.

Even minute traces of moisture apparently lead to formation of some 1,3,5-cyclooctatriene when COT in 2-MTHF is reduced over an alkali metal mirror. This is not immediately obvious in the uv absorption spectrum, but after irradiation 1,3,5,7-octatetraene is formed and interferes badly. The simplest way in which this problem can be avoided is to keep the COT-2-MTHF solution for a day or two at  $-80^\circ$  at the bottom of a sealed vessel containing a metal mirror on the wall above the solution. During this time, a part of the mirror is destroyed, presumably by water vapor. Subsequent contact of the COT-2-MTHF solution with the mirror gives a  $COT^{2-}$  solution without detectable traces of impurities. The  $COT^{2-}$  solutions thus prepared were about  $2 \cdot 10^{-2}$  M in  $COT^{2-}$  and were then diluted by standard techniques for spectroscopic measurements. Break-seals were used for low-temperature addition of further reagents where called for (crown ether).

Authentic samples of 1,3,5,7-octatetraene were prepared by photolysis of 1,3,5-cyclooctatriene,<sup>9</sup> which in turn was prepared from COT.<sup>10</sup>

Absorption spectra were taken with a Cary 17 spectrophotometer. Low-temperature measurements were performed in a Suprasil cell immersed in a Dewar vessel with Suprasil windows filled with liquid nitrogen. Baseline corrections were performed routinely and were important especially in the near-ir region where strong harmonics of solvent ir bands occur.

The emission measurements were done using a 1-kW Xe arc with a regulated power supply, a 100-mm water filter, 250-mm focal length monochromators (Schoeffel Instruments Co.), appropriate focusing mirrors, a Centronics Q4283R photomultiplier with S-20 response, a Keithley Instruments Model 224 power supply, a PAR Model 184 photometric preamplifier, a PAR Model 124 lock-in amplifier, and Omnigraphic Model 2000 Houston Instruments X-Y recorder. Exciting light was chopped at 13 Hz using a PAR Model 125 chopper whose output was used as an external reference for the lock-in amplifier. Front-surface excitation and  $25^\circ$  angle between exciting and emitted beams were used, except in polarized emission measurements, in which the angle was  $90^\circ$ . In the latter measurements, a polarization scrambler was used before the first polarizer to equalize the exciting light intensities in both polarizations. Polacoat polarizing sheets were used as polarizers.

ESR measurements were performed on a standard V-line Varian X-band spectrometer with 100-kHz modulation using a 9-in.

magnet equipped with Fieldial control. The Klystron frequency was about 9.5 GHz for room-temperature measurements and about 9.15 GHz for low-temperature measurements. The latter were performed in a Dewar insert of a Varian variable-temperature accessory. The ESR cavity was a standard universal Varian 104 mode cavity equipped with irradiation slots.

For irradiation of samples, a 200-W high-pressure Hg lamp (PEK) was used in conjunction with a 100-mm water filter, interference filters (narrow band transmission, Balzers, and wide-band reflection, Fish-Shurman), and cut-off filters (Schott). For 254-mm irradiation, a low-pressure Hg lamp (Ultraviolet Products, Inc.) was used without any filters. For shorter wavelength irradiation, Philips metal vapor lamps were used without any filters (Zn, 214 nm; Cd, 229 nm). In order to minimize the effects of destruction of  $COT^-$  by capture of solvent-trapped electrons liberated by excitation with visible light emitted by these lamps, the sample was simultaneously irradiated by a low-pressure Hg lamp.

## Results

**$COT^{2-}$ . Excitation and Emission Spectra.** The uv absorption spectrum of  $COT^{2-}$  has been known for a long time.<sup>11</sup> Even at 77 K (2-MTHF), it is very diffuse. It starts with a weak shoulder near 390 nm and increases to a stronger shoulder near 285 nm (Figure 1). Their exact positions depend slightly on the counterion. We now wish to report observation of emission from rigid solutions of  $COT^{2-}$  in 2-MTHF at 77 K. It is broad and structureless, starts near 400 nm, and reaches a broad maximum near 530 nm. It is unlikely that the emission originates in a species other than  $COT^{2-}$ , not only because of its wavelength, but also since it does not change when the excitation wavelength is changed (310–400 nm), the position of the maximum depends only slightly on the nature of the counterion ( $Na^+$ ,  $K^+$ ,  $Cs^+$ ), and the excitation spectrum (240–400 nm) follows the absorption spectrum of  $COT^{2-}$  at long wavelengths. However, it shows a sudden drop (15–25%) near 335 nm, essentially independently of the nature of the counterion. At shorter wavelengths, it again continues normally, albeit with reduced intensity. The emission is not observed when COT itself is irradiated in 2-MTHF at 77 K.

Since the absorption and excitation spectral curves in-

crease rather rapidly in the vicinity of 340 nm, the sharp drop near 335 nm gives rise to an apparent sharp peak at 340 nm. We have checked carefully that this peak is indeed an inherent feature of the excitation spectrum of  $\text{COT}^{2-}$  (the spectrum is independent of the monitoring wavelength, and emission obtained by excitation at 340 nm is identical with that obtained at other wavelengths).

This sudden decrease in the quantum yield of fluorescence should correspond to the onset of a competing physical or chemical process, and we assign this tentatively as the photoionization process  $\text{COT}^{2-} \rightarrow \text{COT}^- + e^-$  in agreement with the result discussed in more detail below. While irradiation with longer wavelengths is without effect under our experimental conditions, light of  $\lambda \approx 340$  nm or shorter causes electron ejection. The quantum yield of photoionization clearly is much less than one even at quite short wavelengths (250 nm) since, even at these excitation wavelengths, emission is clearly seen. Extended irradiation with 254-nm light destroys all  $\text{COT}^{2-}$  and replaces it by  $\text{COT}^-$  and trapped electrons, as shown by the absorption spectrum and discussed in detail below; at the same time, the green emission attributed here to  $\text{COT}^{2-}$  disappears, providing further support for our assignment. It is unlikely that the emission originates in recombination of photoelectrons with electron traps since quite different emissions were observed with other dianions in 2-MTHF glass.

It should be noted that our absorption, emission, and ionization results for  $\text{COT}^{2-}$  refer to the species predominant in a 2-MTHF solution at 77 K. As is discussed in more detail below, this is the double ion pair  $2\text{M}^+\text{COT}^{2-}$ , with the probable exception of the lithium salt in whose solution several species are apparently present simultaneously in significant concentrations.

**$\text{COT}^-$ . Preparation.** Irradiation of dilute ( $10^{-3}$ – $10^{-5}$  M) glassy solutions of alkali metal salts of  $\text{COT}^{2-}$  in 2-MTHF at 77 K with light of wavelengths approximately 340 nm or shorter (interference filter, 200-W Hg arc) causes disappearance of the uv absorption spectrum of  $\text{COT}^{2-}$  and appearance of the typical broad absorption band of solvated electrons with two maxima near 1200 and 1380 nm and of bands very similar to those reported<sup>5,7</sup> for  $\text{COT}^-$  in the 300–400-nm region (Figure 1). A high degree of conversion can be achieved, quite close to 100% judging by the disappearance of the absorption peak of  $\text{COT}^{2-}$  at 285 nm, where the  $\text{COT}$  spectrum has a minimum. An isosbestic point is observed. In most of our experiments, 254-nm light was used for the photoionization. This wavelength is absorbed strongly by  $\text{COT}^{2-}$  and only weakly by  $\text{COT}^-$ . In the ESR spectrum, the typical easily saturated broad signal of trapped electrons is observed, as well as the seven broad lines of  $\text{COT}^-$  at 3.1-G separation (the outer two lines of the nonet are weak and difficult to observe). An identical ESR spectrum was observed on a frozen sample of a solution containing chemically prepared  $\text{COT}^-$  (see below) and exhibiting a sharp nonet at room temperature (3.15-G splitting).

No apparent changes occur upon standing in the dark at 77 K. Irradiation with visible or near-infrared light, well known to liberate electrons from solvent traps,<sup>12</sup> reduces the bands of the new species in the uv and those of electrons in near-ir and ESR spectra and eventually almost completely restores the spectrum of  $\text{COT}^{2-}$ . Reconversion to  $\text{COT}^{2-}$  can be also achieved by melting the glass. The cycle is almost fully reversible and can be repeated many times.

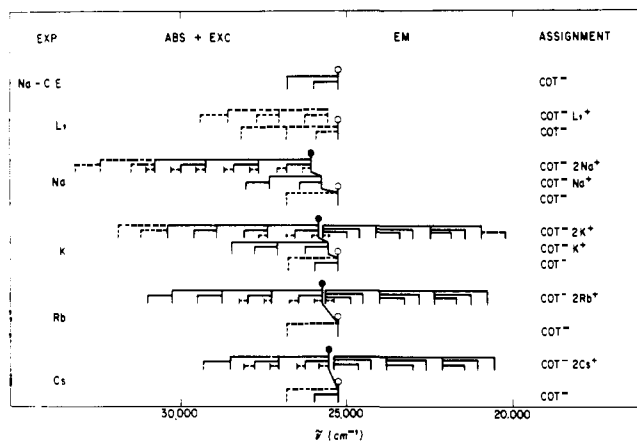
In order to achieve complete conversions to  $\text{COT}^-$ , it is important to use narrow-band uv radiation since visible light liberates electrons from their traps and establishes a photostationary state. After extended periods of irradiation, the total amount of available electrons decreases, presum-

ably due to reaction with solvent, and this apparently causes the observed slight degree of irreversibility in the cyclic process. Trapping of photoejected electrons by dimethyl ether and other ethers under similar conditions has been reported.<sup>12</sup>

Already very small traces of impurities change the behavior of the sample considerably. Uv irradiation of old samples, imperfectly dried samples, and samples prepared with very reactive metals (Rb, Cs) gives mixtures containing 1,3,5,7-octatetraene and at least one red-colored species in addition to  $\text{COT}^-$  and  $e^-(\text{solv})$ . The octatetraene was identified by comparison of its uv, fluorescence, and fluorescence excitation spectra with an authentic sample. We believe that it is formed photochemically from 1,3,5-cyclooctatriene in a well-known reaction.<sup>9</sup> Presumably, in these impure samples some cyclooctatriene is formed by protonation of  $\text{COT}^{2-}$  and its broad absorption band at 265 nm, unlike the sharp peaks of 1,3,5,7-octatetraene, cannot be observed since it is hidden under  $\text{COT}^{2-}$  absorption. The bands in the visible region due to the red-colored species increase considerably upon removal of electrons from their traps by red light (700 nm). Upon subsequent irradiation with blue light (400 nm), the bands of the red-colored species as well as  $\text{COT}^-$  almost disappear, but a band of solvated electrons does not appear. We believe that the red species are radical anions of the olefins present and that red photons do not have sufficient energy to photoionize them while the blue ones do, and that the ejected electrons are trapped by  $\text{COT}^-$  present in large excess. Firm identification of the red species will require further work.

**$\text{COT}^-$ . Ion Pairing.** While the overall appearance of the  $\text{COT}^-$  spectrum depends little on the counterion used, closer inspection reveals significant differences in peak intensities and positions. The intensity of the sharp bands at 320–400 nm relative to the broad peak at 310 nm is high for  $\text{Cs}^+$ ,  $\text{Rb}^+$ , and  $\text{K}^+$  counterions (Figure 1), lower for  $\text{Na}^+$  and  $\text{Li}^+$ , undoubtedly, at least partly because the former have smaller bandwidths. The position of the band origin shifts a few nanometers to the red each time the radius of the counterion increases going down the periodic table ( $\text{Na}^+$ , 383.5;  $\text{K}^+$ , 287;  $\text{Rb}^+$ , 389;  $\text{Cs}^+$ , 392 nm), but the fine-structure spacing remains almost unchanged (Figure 2), confirming that all of the peaks between 320 and 400 nm belong to the same electronic transition, as had been suspected on the basis of calculations.<sup>5</sup>

According to NMR studies, the  $\text{Cs}^+$ ,  $\text{Rb}^+$ ,  $\text{K}^+$ , and  $\text{Na}^+$  salts of  $\text{COT}^{2-}$  exist as doubly contact ion pairs in 2-MTHF at room temperature.<sup>13</sup> They probably also are in this form at 77 K since only one form of the photoproduct is formed initially in our experiments, assigned as  $2\text{M}^+\text{COT}^-$ . However, prolonged irradiation with uv light or very slight softening of the glass reduces its concentration, and a new species appears with identical vibrational structure but an origin shifted slightly to the red. Only one such new form is observed distinctly with  $\text{Cs}^+$  and  $\text{Rb}^+$ , but two of them have been observed with  $\text{Na}^+$  and  $\text{K}^+$  (Figure 2). We propose that the new species are formed by successive diffusion of the counterions away from  $\text{COT}^-$ . Such a process has been observed before on other hydrocarbon anions upon glass softening.<sup>2b</sup> Similarly, we attribute the effect of extended uv irradiation to "internal melting"—conversion of electronic energy of the absorbed quanta into vibrational energy causing local heating and decrease in viscosity. The first peak of the longest wavelength species is at 396 nm irrespectively of the original counterion, and we assign it as the free  $\text{COT}^-$  anion in 2-MTHF solvent. The peak positions are in perfect agreement with those published recently by Shida and Iwata<sup>8</sup> for the free  $\text{COT}^-$  ion in 2-MTHF. The other shifted species is then assigned to the tight ion pair



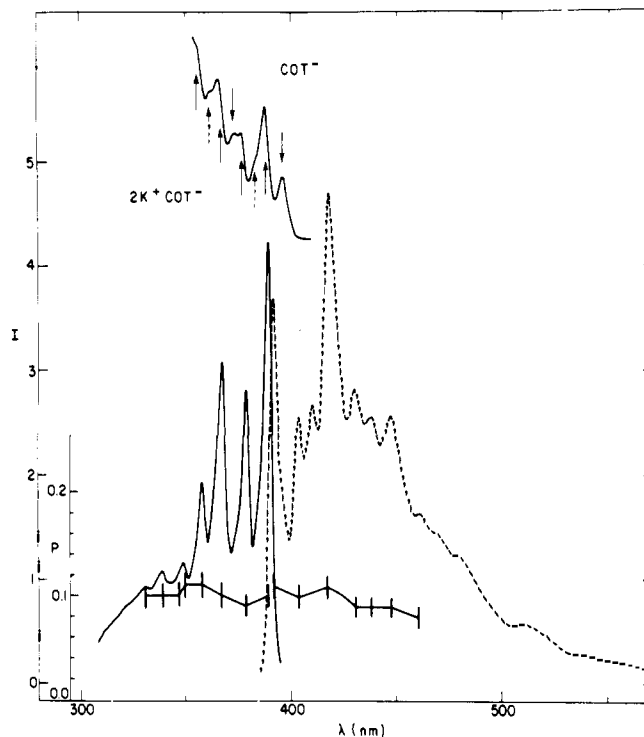
**Figure 2.** Wavenumbers of peaks and shoulders in the absorption (ABS.), excitation (EXC.), and emission (EM.) spectra of  $\text{COT}^-$  in various states of association with cations, measured in 2-MTHF at 77 K. Unclear peaks and shoulders are shown in dashed lines. Metal used for reduction of  $\text{COT}$  is indicated on the left (C.E. = dicyclohexyl-18-crown-6 ether), the assigned state of association on the right. Empty circles indicate the 0-0 absorption peak of "free"  $\text{COT}^-$  obtained in each experiment, full circles that of "doubly tightly paired"  $2\text{M}^+\text{COT}^-$ .

$\text{M}^+\text{COT}^-$  ( $\text{Na}^+$ , 388.5;  $\text{K}^+$ , 391.5 nm). It has not been observed for  $\text{Rb}^+$  and  $\text{Cs}^+$ , and this can be understood since the magnitude of the spectral shifts between the various forms decreases with increasing cation size, and the spectral observation becomes more difficult. Indeed, for several of the species, only the first peak in the spectrum can be distinctly observed. In incompletely reduced solutions containing both  $\text{COT}^{2-}$  and  $\text{COT}^-$ , and in aged solutions, the 396-nm peak assigned to free  $\text{COT}^-$  appears already from the beginning of the irradiation. We assign this to trapping of some of the photoejected electrons by  $\text{COT}$  present.

In principle, a great variety of species should be possible, combining tight or loose pairing of the two counterions or possibly an even larger number of possibilities,<sup>14</sup> but we assume that only tight pairing affects absorption spectra (cf. ref 4a). Thus, whenever we refer to an ion pair, a tight pair is meant, and no claims are made concerning loose pairing.

Although NMR results<sup>13</sup> indicate that the  $\text{Li}^+$  salt of  $\text{COT}^{2-}$  also exists only as  $2\text{Li}^+\text{COT}^{2-}$  tight pair in ether solvents at room temperature, it apparently exists as a mixture of several ion-paired species at 77 K in 2-MTHF, since several forms of the photoproduct are formed initially upon photoionization. This is not unreasonable, since it is well known that a decrease in temperature, as well as a decrease in the cation radius, promote ion-pair dissociation. The simultaneous presence of several species makes spectral analysis very difficult. Tentative results are indicated on top of Figure 2. All of the peaks shown are present initially. The indicated assignment to a mixture of free  $\text{COT}^-$  and  $\text{Li}^+\text{COT}^-$  only, with no  $2\text{Li}^+\text{COT}^-$ , is not certain, since extrapolated position of the first peak of  $2\text{Li}^+\text{COT}^-$  (26 300  $\text{cm}^{-1}$ ) coincides with one of the observed peaks assigned as a vibrational sublevel in the spectrum of  $\text{Li}^+\text{COT}^-$ .

**$\text{COT}^-$ . Fluorescence.** The species first formed from  $\text{Cs}^+$ ,  $\text{Rb}^+$ , and  $\text{K}^+$  salts of  $\text{COT}^{2-}$ , believed to have structure  $2\text{M}^+\text{COT}^-$ , exhibit strong structured fluorescence (Figures 2 and 3). The excitation spectra follow the details of the absorption spectra between 400 and about 350 nm, but gradually fall off at shorter wavelengths, and excitation into the strong peak at 310 nm causes virtually no emission. In all three cases, the 0-0 components of absorption and fluorescence coincide and are relatively strong, showing that the transition is symmetry allowed. The vibrational features of the fluorescence and absorption do not change with the



**Figure 3.** Excitation (solid line) and emission (dashed line) spectra of  $2\text{K}^+\text{COT}^-$  in 2-MTHF at 77 K. Intensity ( $I$ ) in arbitrary units, not corrected for instrumental response. Vertical lines in the lower part and insert scale on the left: polarization degree ( $P$ ) (error limits estimated). On top, absorption spectrum of a mixture of  $2\text{K}^+\text{COT}^-$  (arrows from the bottom) with  $\text{COT}^-$  (arrows from the top) obtained by irradiation of  $2\text{K}^+\text{COT}^{2-} + \text{COT}^-$  mixture (bottom wavelength scale applies). Excitation spectrum of the mixture is identical with that shown below (free  $\text{COT}^-$  does not emit).

counterion and are fairly close, but not perfect, mirror images of each other. The fluorescence can be analyzed in terms of four vibrational frequencies. It contains four progressions in a  $1590\text{ cm}^{-1}$  vibration built on four origins. One of these is the 0-0 band, and the others are obtained by adding one quantum of 250-, 750-, and  $1120\text{-cm}^{-1}$  vibrations. The combinations involving the  $250\text{-cm}^{-1}$  vibration appear only as very weak shoulders, and the error in the determination of its wavenumber is estimated as  $\pm 50\text{ cm}^{-1}$ ; the error in the other three vibrations is estimated as  $\pm 20\text{ cm}^{-1}$ .

In absorption (and excitation) spectra, the vibrational structure is simple since only three vibrations are discerned. The progression-forming vibration is  $1520\text{ cm}^{-1}$ , and the origins are the 0-0 band, 0-0 +  $300\text{ cm}^{-1}$ , and 0-0 +  $720\text{ cm}^{-1}$ . Combinations involving the  $300\text{-cm}^{-1}$  vibration appear only as weak shoulders (error  $\pm 50\text{ cm}^{-1}$ ); the error limits estimated for the 720- and  $1520\text{-cm}^{-1}$  vibrations are  $\pm 30$  and  $\pm 20\text{ cm}^{-1}$ , respectively. The relatively strong  $1120\text{-cm}^{-1}$  frequency of the emission has no observable counterpart in absorption, but this might simply be due to limited resolution if it occurs with low intensity.

In spite of considerable effort, no emission from otherwise ion-paired species nor from any  $\text{Li}^+\text{COT}^-$  and  $\text{Na}^+\text{COT}^-$  samples was found. The absence of such emission turned out to be quite helpful for analysis of mixtures containing several species simultaneously (Figure 3).

Polarization of the excitation and emission spectra is constant within experimental error, just below  $1/7$  (Figure 3). This low value is not an instrumental artifact since measurements in the presence of accumulated 1,3,5,7-octatetraene give polarization ratios around 0.4 for its emission

and excitation, near the theoretical value of 0.5, but still give only less than 1/7 for the polarization ratio in the emission and excitation of the  $\text{COT}^-$  which is also present. This result shows that absorption and emission are polarized in a plane rather than along a line,<sup>15</sup> and thus the transition involves a degenerate state within the resolving power of our instrumentation. The molecule and its associated counterions must therefore have at least a threefold proper or improper symmetry axis on the time scale of the fluorescence lifetime. Combined with the formula  $2\text{M}^+\text{COT}^-$ , this result requires a fourfold or eightfold axis.

**$\text{COT}^-$ . Attempted Ionization.** The photoionization of  $\text{COT}^{2-}$  to  $\text{COT}^-$  at 77 K proceeds well with light of wavelengths below 340 nm, but no further ionization to  $\text{COT}$  has been detected with 254-nm light for which the 2-MTHF glass is still quite transparent nor 229- and 214-nm light for which at least some reaction near the surface might have been expected. An attempt was made to facilitate the photoionization by "loosening" the tightly paired counterions. Unfortunately, addition of dicyclohexyl-18-crown-6 ether<sup>16</sup> to  $\text{Na}_2\text{COT}$  in 2-MTHF leads to a chemical reaction accompanied by a formation of a yellowish precipitate and red solution. A similar result is obtained when a solution of  $\text{COT}$  and crown ether in 2-MTHF is reduced over potassium mirror. The basicity of free  $\text{COT}^{2-}$  is apparently extremely high. These reactions were not investigated in detail. We also attempted to prepare free  $\text{COT}^-$ , which should be much less reactive than  $\text{COT}^{2-}$ , by mixing a solution of  $\text{Na}_2\text{COT}$  in 2-MTHF with an equimolar solution of  $\text{COT}$  and the crown ether (3%) in 2-MTHF at  $-50^\circ\text{C}$ . Indeed, the weakly blue resultant mixture gave the expected ESR spectrum, which persisted for weeks at room temperature. Free  $\text{COT}^-$  is known<sup>6,7</sup> to give a sharp nonet [peak-to-peak line width 0.06 G (derivative), splitting constant 3.17 G], while for the  $\text{Na}^+\text{COT}^-$  ion pair the reported line width is 0.40 G and  $\text{Na}$  hfsc is 0.96 G. Our spectrum was a nonet (peak-to-peak line width 0.30 G, hfsc 3.15 G) with very faint indications of unresolved splitting by sodium (hfsc  $< 0.1$  G). This appears reasonable for a weak crown ether- $\text{Na}^+\text{COT}^-$  complex.<sup>17</sup> When the ESR spectrum is taken in a rigid solution at 77 K, it is identical with that obtained from photoionization experiments as described above. Uv and visible spectra show that the solution is a complicated mixture,<sup>18</sup> and the bands of  $\text{COT}^-$  can be hardly discerned. Those that can be identified agree with those of free  $\text{COT}^-$  obtained as described in the preceding section. Over a period of several days at room temperature, the blue color of the solution progressively darkens, indicating further decomposition. Nevertheless, attempts to observe photoionization were made on both fresh and aged solutions, but the only obvious change in the uv spectrum was formation of a large amount of 1,3,5,7-octatetraene. It is not clear how much of the light was actually absorbed by  $\text{COT}^-$  in this complicated mixture. No half-field signal attributable to a triplet was observed in the ESR spectrum in spite of repeated attempts. An attempt to prepare a solution of  $\text{COT}^-$  in another glass-forming solvent, 3-methylpentane containing 3% Cryptate,<sup>20</sup> by reduction of  $\text{COT}$  over a potassium mirror failed, and only an insoluble blue sticky solid resulted. Attempts to observe further photoionization of the free  $\text{COT}^-$  anion obtained by cation diffusion from initially prepared  $2\text{M}^+\text{COT}^-$  clusters, as described in the preceding section, in the presence or absence of neopentyl chloride or excess  $\text{COT}$  as electron traps<sup>21</sup> gave no indication of a new species in absorption spectra (the spectrum of ordinary  $\text{COT}$  is so weak and diffuse that it would not have been noticed until quite high degree of conversion was reached), although in some instances a weak signal in the half-field region typical of triplets was observed.

## Discussion

The observation of emission from  $\text{COT}^{2-}$  is somewhat of a surprise, since to our knowledge fluorescence from hydrocarbon double anions has not been recorded before in the literature, and it seemed reasonable to expect all excited states to autoionize efficiently. More recently, we have observed fluorescence from other hydrocarbon double anions as well. It appears that ion pairing increases the ionization threshold energy considerably. This threshold is ordinarily deduced from the wavelength required for ionization to take place; our observation of a drop in the fluorescence excitation spectrum provides a complementary and somewhat more accurate estimate of this value (3.7 eV in 2-MTHF at 77 K). The lack of counterion effect on this value probably only reflects the limited accuracy of our results. A more detailed comparison of the two types of measurement would be desirable but would require a more monochromatic intense light source for photoionization, such as a tuneable laser, which unfortunately was not at our disposal.

The formation of  $\text{COT}^-$  upon photoionization proceeds as expected and reinforces our belief that assignment of species obtained by photoionization of similar but less well studied hydrocarbon double anions, such as the pentalene dianion,<sup>3b</sup> as radical anions, is quite safe in those instances in which reversal of the ionization process by heating or irradiation leads back to the initial dianion.

A considerable amount of new information was obtained about the  $\text{COT}^-$  anion. From the fact that the fine structure in the 300–400-nm region moves as a whole upon slight perturbation, we conclude that all of it belongs to a single electronic transition. The relatively sharp vibrational structure in absorption and in emission indicates that  $\text{COT}^-$  is planar and fairly rigid, at least in form of some of its ion clusters. Combined with the presence of an approximate mirror-image symmetry between emission and absorption and with the intensity of the 0–0 band relative to others, this indicates that the rigidity and planarity are preserved in the lowest excited state, whose shape apparently differs only little from that of the ground state.

The electronic states of  $\text{COT}^-$  have been discussed by numerous authors. Most of the attention was directed to the ground state,<sup>22</sup> but three groups of authors have performed  $\pi$ -electron calculations on excited states as well.<sup>5,8,23</sup> It is generally assumed on basis of polarographic,<sup>19</sup> ESR,<sup>7</sup> and gas-phase electron attachment<sup>24</sup> studies that the anion deviates only little, if at all, from the regular octagonal geometry ( $D_{8h}$ ), although MINDO calculations slightly favor a nonplanar geometry.<sup>22</sup> Some deviation in the sense of a  $b_{2g}$  vibration is expected at any rate according to the Jahn-Teller theorem (slight alternation of bond lengths). Another distortion which could, in principle, be used in a Jahn-Teller effect is  $b_{1g}$ , which would move alternate carbon atoms radially in and out. Such bending vibrations are less effective than stretching vibrations and only insignificant  $b_{1g}$  distortion apparently occurs (nonuniform spin density would otherwise be expected, but is not observed).<sup>7,25</sup> The Jahn-Teller stabilization due to  $b_{2g}$  distortion has been calculated<sup>25</sup> as approximately  $700\text{ cm}^{-1}$ , comparable with zero-point energy of the  $b_{2g}$  vibration (dynamic Jahn-Teller effect).

Since the molecule spends most of its time very near the  $D_{8h}$  geometry, calculations at this geometry should represent a reasonable starting point for an analysis of excited states. At this geometry, the  $\pi$ -electron MO's are  $a_{2u}$ ,  $e_{1g}$ ,  $e_{2u}$ ,  $e_{3g}$ , and  $b_{2u}$  in the order of increasing energy, and the lowest configurations are  $a_{2u}^2e_{1g}^4e_{2u}^3$ ,  $a_{2u}^2e_{1g}^3e_{2u}^4$ , and  $a_{2u}^2e_{1g}^4e_{2u}^2e_{3g}^1$ . The first of these gives rise to the  ${}^2E_{2u}$  ground state, the latter two to three  ${}^2E_{1g}$  and two  ${}^2E_{3g}$

states. These should account for low-lying excited states of  $\text{COT}^-$  at  $D_{8h}$  geometry. Both  ${}^2E_{1g} \leftarrow {}^2E_{2u}$  and  ${}^2E_{3g} \leftarrow {}^2E_{2u}$  transitions are electric dipole allowed, and one or more quanta of  $a_{1g}$ ,  $a_{2g}$ ,  $b_{1g}$ ,  $b_{2g}$ , and  $e_{2g}$  vibrations may appear, in any combination. The following skeletal vibrations are available:  $a_{1g}$  ring breathing,  $b_{1g}$  CCC in-plane bend,  $b_{2g}$  C-C stretch,  $e_{2g}$  C-C stretch, and  $e_{2g}$  CCC in-plane bend.

Numerical results are required to estimate the order and energies of the excited states. Those obtained by previous authors<sup>5,8,23</sup> using  $\pi$ -electron methods with the zero-differential overlap approximation are in reasonable agreement with experiment, particularly now that it has been shown that all of the observed structure between 360 and 400 nm can be assigned to a single transition. The information available at present does not permit an assignment of the four observed vibrational spacings to the five vibrational frequencies allowed in principle.

We have performed some additional calculations by a semiempirical all-valence electron method<sup>26</sup> which avoids zero differential overlap and uses the Mulliken approximation for multicenter integrals, but the results (first transition at 394 nm, second transition at 289 nm) essentially only confirm those of earlier authors<sup>5,8,23</sup> and will not be discussed in detail.

The observation of strong fluorescence is interesting in view of relative scarcity of recorded emissions from hydrocarbon anions.<sup>27-29</sup> The presence of observable fluorescence for some ion-paired species and absence for other closely related ones is quite striking. A related observation has been published by Burley and Young,<sup>27</sup> who observed emission from a free but not ion-paired anion. The quenching mechanism involved is presently not understood. Some of the factors possibly involved are (i) decreased rigidity or even non-planarity of some of the ion pair forms of  $\text{COT}^-$  compared to others, (ii) the relative position of the lowest excited doublet state and the lowest  ${}^4E_{3g}$  quartet state, expected<sup>23</sup> to be of a similar energy, (iii) differences in energy and other properties of charge-transfer states corresponding to transfer of an electron from  $\text{COT}^-$  to  $\text{M}^+$ . The rapid fall-off of the fluorescence excitation spectrum at wavelengths shorter than about 350 nm for those ion pairs which do emit is only partly due to decreased lamp output in this region and is also unusual. Since continued irradiation at this wavelength does not cause visible photochemical changes other than gradual diffusion of the counterion away from  $\text{COT}^-$ , some similar quenching mechanism may be involved.

The result of measurement of polarized emission and excitation on  $2\text{M}^+\text{COT}^-$  is in good agreement with  $D_{8h}$  geometry, but it does not exclude certain lower symmetries such as  $D_{4h}$ . It does show, however, that the counterions are located on the fourfold or eightfold symmetry axis in the rigid solution, and this then most likely also is the lowest energy configuration of  $2\text{M}^+\text{COT}^{2-}$  in fluid solution at room temperature. This arrangement appears reasonable from simple electrostatic considerations and by comparison with recently published crystal studies<sup>30</sup> of salts of  $\text{COT}^{2-}$  and its tetramethyl derivative.

Effects of tightly paired counterions on the excitation energies of anions have been observed many times before and are usually attributed to electrostatic effects.<sup>31</sup> Our case is interesting in that a series of ions of the type  $2\text{M}^+\text{A}^-$  is available along with the more usual pairs  $\text{M}^+\text{A}^-$ , and in that the sharpness of the peaks permits a relatively accurate determination of the shifts.

The shifts per cation are about half of those observed in the fluorenone anion.<sup>4a</sup> They are not quite linear when plotted against  $1/R$ ,<sup>4a</sup>  $1/(R+2)$ ,<sup>31</sup> or other similar functions ( $R$  is the covalent radius of the cation), perhaps because weak specific interactions between orbitals of  $\text{COT}^-$  and

those of  $\text{M}^+$  are superimposed on the "ordinary electrostatic" effects.

Two final remarks: It has been reported some time ago<sup>32</sup> that uv irradiation of  $\text{COT}^{2-}$  apparently increases its basicity, since incorporation of deuterium from 1-hexyne-1- $d_1$  present in the solution occurs upon irradiation but not in the dark. While a simple protonation mechanism certainly is a possibility, it should be kept in mind that this and other photoreactions of anions may also involve electron photoejection as a reaction step or as a sidetrack. Finally, our failure to observe a planar  $\text{COT}$  triplet deserves mention. We feel that the approach chosen here may yet lead to the goal; two most likely reasons for our lack of success are insufficient photon energy (limited by the solvent used) and too short a lifetime of the planar triplet under our experimental conditions.

**Acknowledgment.** The authors are indebted to Dr. H. K. Frensdorff and Dr. D. J. Sam (du Pont de Nemours and Co., Inc.) for a generous gift of crown ether, to Professor P. D. Gardner, who kindly provided a sample of Cryptate, and to Professor F. E. Harris (both from the University of Utah) for permission to use his all-valence-electron program. The work was supported by the Research Foundation, the Alfred P. Sloan Foundation (fellowship to J. M.), and, in part, by the National Science Foundation (GP-37 551).

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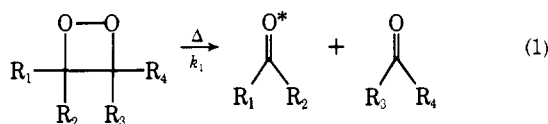
## Thermolysis of Tetramethoxy- and *p*-Dioxenedioxetanes. Kinetic Parameters, Chemiluminescence, and Yields of Excited Products

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**Abstract:** The kinetic parameters of the first-order thermal decompositions of tetramethoxy- (**1**) and *p*-dioxenedioxetanes (**2**) were determined (in benzene or xylene solutions) and compared, using the same experimental methods, with those of tetramethyl- (**3**) and *cis*-diethoxydioxetanes (**4**). **1** is much more stable than **3**. The activation energies of these two thermolyses are nearly the same; hence the greater stability of **1** is largely due to a smaller *A* factor ( $E_a = 28.6$  kcal,  $\log A = 12.9$  for **1**;  $E_a = 27.6$  kcal,  $\log A = 14.1$  for **3**). **2** is slightly more stable than **4** although their activation energies are the same,  $E_a \approx 24.5$  kcal ( $\log A = 13.0$  for **2**; 13.6 for **4**). The last result indicates that the 3–4 kcal strain of the ester ring of **2** is released after the transition state is attained, suggesting that the decomposition proceeds via a diradical pathway. Quantum yields of excited singlet and triplet products ( $^1\phi$  and  $^3\phi$ ) were determined on the basis of chemiluminescence intensities with 9,10-diphenyl- or 9,10-dibromoanthracene. The yields from **2** ( $^1\phi = 0.0001$  and  $^3\phi = 0.3$ ) are very similar to those obtained with **3** and **4**. With **1**, in contrast,  $^1\phi = 0.01$  and  $^3\phi = 0.1$ , showing a lower total yield of excited products, but a higher production of singlets. Quenching experiments with dienes, from which excited carbonyl lifetimes are derived, support these results.

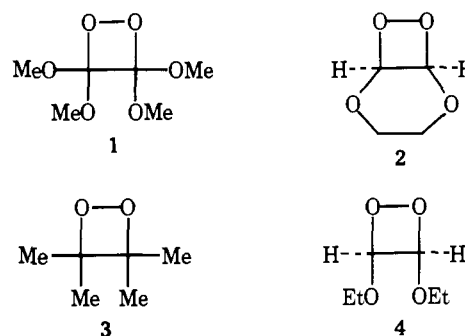
The thermal cleavage (eq 1) of all isolated dioxetanes has been shown to generate excited carbonyl products,<sup>1</sup> generally favoring triplet over singlet states.



The nature of the substituents on the ring has relatively little effect on the dioxetane's properties. Whether the dioxetane is substituted by one or by several methyl or phenyl groups, for example, its stability remains much the same ( $E_a \approx 25 \pm 2$  kcal,  $\log A = 13 \pm 1$ ),<sup>2</sup> although bulky rigid groups (as in adamantylideneadamantanedioxetane,  $E_a \approx 37$  kcal) render the dioxetane considerably more stable.<sup>3</sup>

On the other hand, the hypothetical dioxetanes, assumed to be the precursors of excited products in many classic cases of intense chemiluminescence,<sup>4</sup> must be considerably less stable and capable of generating more singlet excited products. Thus it is clear that appropriate substitution should not only decrease the stability of the dioxetane, but might also upset the balance of excited products in favor of singlets rather than triplets.

The effect of well-chosen substituents should also throw light on the much debated mechanism of reaction 1, concerted vs. diradical, and on excitation pathways. Two previously synthesized dioxetanes, tetramethoxydioxetane<sup>5</sup> (**1**) and *p*-dioxenedioxetane<sup>18,6</sup> (**2**), were investigated and their properties compared with those of tetramethyldioxetane (**3**)



and *cis*-diethoxydioxetane (**4**); the same experimental methods were used in all cases. **2** is of interest because, while similar to **4**, its second ring has an appreciable strain. In **1** the effect of alkoxy substituents can be compared with that of the methyl groups of **3**. The results are interpreted as favoring a diradical mechanism; they emphasize the importance of entropy effects on the stability of the dioxetanes.

### Experimental Section

Tetramethoxydioxetane was prepared by low-temperature photooxygenation of tetramethoxyethylene essentially as described by Mazur.<sup>7</sup> The dioxetane was recrystallized at  $-78^\circ$  from pentane to yield a light-yellow solid. The pure dioxetane, a liquid at room temperature, was rapidly dissolved in either benzene-*d*<sub>6</sub> or acetone-*d*<sub>6</sub> for storage at  $-20^\circ$ . The dioxetane concentration was de-