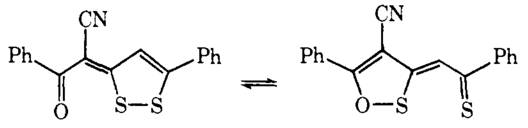
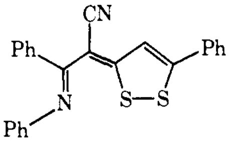
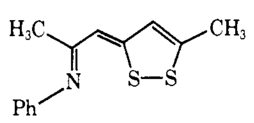
X-ray measurement will still yield a symmetric density map with a reduced temperature factor compared with that of the situation in Figure 2c.

(2) For an unsymmetric molecule, *e.g.*, IIa, one should be able to obtain the valence tautomer in a photochemical reaction (see Figure 2d). To test this latter prediction, we have carried out a flash experiment with IIa, III, IV, and V. We used a 900-J flash (30 kV, 2μF), with WG1 and GG455 Schott filters. The measurements were done in cyclohexane and ethanol at room temperature in the presence and absence of air.

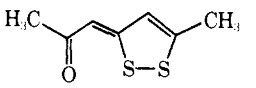




III



IV

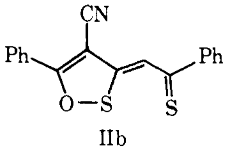


V

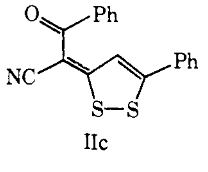
Irradiation of IIa yields two products in cyclohexane. In Figure 3, we show the electronic spectrum of IIa and the spectrum of the second longer lived product, which reverts in a dark reaction. The change in optical density which accompanies the reaction at wavelengths from 300 to 500 nm obeys first-order kinetics. No stable products were detected under these conditions. In cyclohexane, the electronic spectrum of the photoproduct of IIa is similar to that in ethanol: maxima at 470 and 305 nm, isosbestic points at 455, 415, and 350 nm. The relaxation time at room temperature is 300 sec in cyclohexane and 0.1 sec in ethanol.

Compounds III, IV, and V show behavior similar to that of IIa. The decay of the longest lived product obeys first-order kinetics. The relaxation times for the different compounds in cyclohexane are 350 sec for III, 240 sec for IV, and 670 sec for V. The estimated standard error is about 15%, taken from six measurements. The measurements also show that there is a similar bathochromic shift of the first band in the electronic spectrum as observed for IIa.

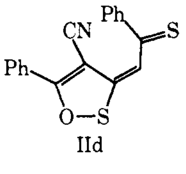
From the facts that the long-lived product reverts into the starting material according to a first-order kinetics, that there is a bathochromic shift of the first $\pi^* \leftarrow \pi$ band relative to that of the starting product, and that air does not influence the lifetime of the product, we conclude that this species is a singlet isomer of the starting material. For IIa we have taken into consideration three isomers, IIb, c, d. As was pointed out previously,[1] the position of the band which corresponds to a $\pi^* \leftarrow \pi$ transition of lowest energy allows one to discriminate between the structures of different isomers like IIa–IId. We have carried out PPP calculations[11] on the four unsubstituted isomers a–d corresponding to IIa–IId. We obtained a shift of the long-wavelength band relative to the position of a as follows: b = +48, c = −51, and d = −16 nm. It is obvious that only isomer b is compatible with the bathochromic shift as observed in our measurements. The size of this calculated shift corresponds to the measured one of 30 nm for the photoproduct of IIa in cyclohexane. This result is supported by the observation that the known trans isomers[12] corresponding to structure c show a hypsochromic shift of the first $\pi^* \leftarrow \pi$ band of about 50–60 nm relative to the a isomer. The observed solvent shift is also in agreement with isomer b. Hydrogen bonding in ethanol should lower the stability of the S–O bond, and thus the lifetime of the tautomer IIb should be smaller than in cyclohexane, which is observed.



IIb



IIc



IId

We conclude that the longest lived product encountered in our experiments is in each case the valence tautomer of the starting material.

Acknowledgment. This work is part of project No. SR 2.120.69 of the Schweizerischer Nationalfonds. We wish to thank Sandoz AG (Basel) for computer time.

---

(11) R. Zahradnik, *Fortschr. Chem. Forsch.*, **10**, 1 (1967); J. Fabian, A. Mehlhorn, and R. Zahradnik, *J. Phys. Chem.*, **72**, 3975 (1968).

(12) H. Behringer, *Chimia*, **19**, 132 (1965); H. Behringer and U. Hrabal, manuscript in preparation.

Rolf Gleiter,* Dietrich Werthemann
Physikalisch-Chemisches Institut der Universität Basel
Basel, Switzerland

Hans Behringer
Institut für Organische Chemie der Universität München
Munich, Germany

Received June 10, 1971

Molecular Oxygen Binding in a Monomeric Cobalt Complex. The Crystal and Molecular Structure of Dioxygen–Bis[*cis*-1,2-bis(diphenylphosphino)ethylene]cobalt Tetrafluoroborate

Sir:

We report the structure of the title compound $[O_2\text{-}Co(2{=}phos)_2]BF_4$ where (2=phos) is *cis*-$[(C_6H_5)_2PCH{=}CHP(C_6H_5)_2]$ containing two benzene molecules of solvation. This represents the first announcement of a structure determination of a synthetic monomeric O_2 complex with a metal of the iron triad. Several structure investigations of oxygenated Co complexes have been reported;[1-3] these have all been O_2 bridged dimers, which are well-known oxygen carriers.[4]

The oxygen adduct is prepared by exposing either the crystalline material or solutions of the planar Co(I) chelate, $[Co(2{=}phos)_2]^+BF_4^-$,[5] to atmospheric oxygen.

---

(1) W. P. Schaefer, *Inorg. Chem.*, 7, 725 (1968).

(2) M. Calligaris, G. Nardin, and L. Randaccio, *Chem. Commun.*, 763 (1969).

(3) M. Calligaris, G. Nardin, L. Randaccio, and A. Ripamonti, *J. Chem. Soc. A*, 1069 (1970).

(4) R. G. Wilkins, *Advan. Chem. Ser.*, **No. 100**, 111 (1970).

(5) L. Vaska, L. S. Chen, and W. V. Miller, *J. Amer. Chem. Soc.*, **93**, 6671 (1971).

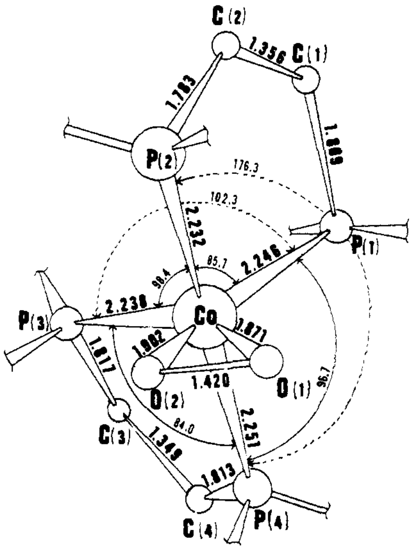


Figure 1. A perspective view of the $[O_2Co(2 = phos)_2]^+$ ion indicating important distances and angles. The phenyl rings are not shown for reasons of simplicity. The "equatorial" plane is defined by P(3), P(1), and midpoint of O(1)–O(2). Estimated standard deviations for Co–P, Co–O, O–O, P–C, C–C are ±0.003, ±0.007, ±0.010, ±0.011, ±0.015 Å or less, respectively; and the P–Co–P angle ±0.1°.

The O_2 complex is diamagnetic, monomeric in $CHCl_3$, and behaves as a uni-univalent electrolyte in acetone. Its infrared spectrum shows a characteristic ν_{CoO_2} band at 909 cm^{-1} in $CHCl_3$. Diffraction-quality single crystals were grown from benzene–dichloromethane solutions. Crystal data: λ 0.71068 Å, $P2_1/c$, a = 16.034 (6) Å, b = 18.186 (9) Å, c = 19.721 (8) Å, β = 101.20 (1)°, Z = 4, $[O_2Co(2{=}phos)_2]^+BF_4^- \cdot 2C_6H_6$, ρ_{calcd} = 1.35 g cm^{-3}, ρ_{obsd} = 1.33 g cm^{-3}. A crystal in the approximate shape of a distorted, elongated, tetragonal pyramid with dimensions 0.33 × 0.36 × 0.57 mm was sealed into a capillary tube with the long direction approximately parallel to the capillary length and used for data collection and absorption corrections.[6] The crystal was aligned by standard techniques[7] on a Picker FACS-1 automated diffractometer equipped with a graphite monochromator. By standard θ–2θ scanning techniques 14,189 independent hkl reflections were measured, of which 4296 were considered statistically nonzero. The structure was solved by standard heavy atom techniques and refined by full-matrix least squares with weights determined by counting statistics.[7] Anomalous dispersion corrections were included for Co and P. Only the Co, P, and O thermal parameters were refined anisotropically. The phenyl rings were refined as rigid groups. The final R, weighted R, and standard error were found to be 0.066, 0.069, and 0.53.[7]

The structure may be described as composed of molecular ions of the oxygenated Co chelate and BF_4^- ions with only normal van der Waals distances between the moieties and solvent molecules filling the voids. The structure of $[O_2Co(2{=}phos)_2]^+$ is seen in Figure 1 and for geometric representation may be regarded as a distorted trigonal-bipyramidal configuration for Co, with the O_2 molecule in the equatorial plane and its molecular center defining a coordination site. The gross structural features are similar to those found for $[O_2Rh(diphos)_2]^+$ and $[O_2Ir(diphos)_2]^+$.[8] In fact, if the C(1)–C(2) and C(3)–C(4) bonds are severed as well as the analogous bonds in the $[O_2M(diphos)_2]^+$, M = Rh and Ir, they can all be related to $[O_2IrX(CO)(R_3P)_2]$ structures: R = Ph, X = Cl;[9] R = Ph, X = I;[10] $2R_1$ = Ph and R_2 = Et, X = Cl;[11] R = Ph, X = Br.[12] For example, the P(2)–M–P(4) angle is always ~175°, less than linear. The Co–O distances of 1.871 (7) and 1.902 (7) Å are significantly shorter than the previously reported Ir–O and Rh–O distances. However, if one assumes M–O single bonds, this decrease is as expected from covalent radii. The O–O distance in the cobalt complex, 1.420 (10) Å, is essentially identical with that found in $[O_2Rh(diphos)_2]^+$, 1.418 (11) Å,[8] and comparable to those in $[O_2IrCl(CO)(Ph_2EtP)_2]$, 1.461 (14) Å,[11] and $[O_2IrBr(CO)(Ph_3P)_2]$, 1.36 (4) Å.[12] It is noteworthy that the oxygen binding to the latter three compounds is reversible at 30–60°,[13] while the oxygen uptake by $[Co(2{=}phos)_2]^+$ is essentially irreversible under the same conditions.[5] Furthermore, the O–O distances in $[O_2IrCl(CO)(Ph_3P)_2]$, $[O_2IrI(CO)(Ph_3P)_2]$, and $[O_2Ir(diphos)_2]^+$ are 1.30 (3),[9] 1.526 (26),[10] and 1.625 (23) Å,[8] respectively. The deoxygenation of the chloro complex is facile, whereas that of the latter two complexes is not.

There are several possible modes of description of the bonding in $[O_2Co(2{=}phos)_2]^+$ making use of the geometry above and the diamagnetism. Although the geometry has been described in terms of a trigonal-bipyramidal arrangement, it is equally valid to think of it as a distorted six-coordinate metal with two metal–oxygen bonds. Descriptions of the bonding in terms of O_2^{2-}–Co(III) (d^6) or O_2^-–Co(II) (d^7) represent localized models of a much more flexible situation, *i.e.*, a delocalized three-center molecular orbital involving $d_{(x^2-y^2)}$ or d_{xy} (degenerate under D_{3h}) and an in-plane π^* of O_2. Therefore, conventional coordination numbers and integral oxidation states are inadequate for the discussion of the bonding in these types of covalent compounds;[14] any discussion of the covalent bonding in these types of oxygen adducts must take due cognizance of the M–O binding as well as the O–O binding. The determinations of the crystal structures of the Rh and Ir analogs are in progress.

Acknowledgment. We thank Mr. L. S. Chen for the preparation of the crystals, Dr. W. V. Miller for magnetic measurements, Dr. W. A. Spofford, III, and A. G. Gash for computer programming, the National Institutes of Health, Grant No. HE-9678 (L. V.) and

---

(6) Absorption corrections made with a local version of GONO-9, originally written by W. C. Hamilton.

(7) For alignment procedure, computer programs, source of scattering factors, weighting scheme, and other routine information, see R. L. Girling and E. L. Amma, *Inorg. Chem.*, **10**, 335 (1971); final refinement carried out with a version of the computer program described in the above paper but on the CDC 6600.

(8) J. A. McGinnety, N. C. Payne, and J. A. Ibers, *J. Amer. Chem. Soc.*, **91**, 6301 (1969).

(9) S. J. La Placa and J. A. Ibers, *ibid.*, **87**, 2581 (1965).

(10) J. A. McGinnety, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 2243 (1967).

(11) M. S. Weininger, I. F. Taylor, Jr., and E. L. Amma, *Chem. Commun.*, 1172 (1971).

(12) W. A. Spofford, III, and E. L. Amma, unpublished results.

(13) (a) L. Vaska and L. S. Chen, *Chem. Commun.*, 1080 (1971); (b) L. Vaska, L. S. Chen, and C. V. Senoff, *Science*, 174, 587 (1971).

(14) L. Vaska, *Accounts Chem. Res.*, **1**, 335 (1968).

HE-12523 (E. L. A.), for support, and NSF GP-18507 for instrumentation.

N. W. Terry, III, E. L. Amma*
Department of Chemistry, University of South Carolina
Columbia, South Carolina 29208

L. Vaska
Department of Chemistry, Clarkson College of Technology
Potsdam, New York 13676

Received September 16, 1971

Rate of the Self-Quenching Reaction for Thioxanthone Triplets

Sir:

The choice of a sensitizer for a photochemical reaction can often be of critical importance. It has been pointed out that the absorption spectrum, the intersystem crossing ratio, and the triplet energy all need to be considered in the choice of a sensitizer for a given reaction.[1] To these may be added the consideration of the self-quenching reaction (eq 1), which has recently been reported for Michler's ketone,[2] thioxanthone,[3] and various alkoxy-substituted acetophenones.[3]

$$^3\text{sensitizer} + {}^0\text{sensitizer} \xrightarrow{k_q} {}^3\text{complex} \longrightarrow \text{products} \qquad (1)$$

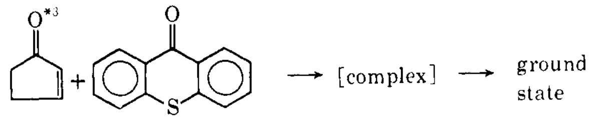
The rates for the self-quenching reactions reported in the literature are given in Table I. They range from 9 × 10^7 l./(mol sec) for *p*-methoxyacetophenone to 6 × 10^{10} l./(mol sec) for thioxanthone. The latter value is larger than that for a diffusion-controlled reaction and would imply a long-range mechanism for the self-quenching reaction rather than complex formation as shown in eq 1. The existence of such a long-range quenching mechanism would have serious theoretical consequences as well as the practical one of rendering thioxanthone unfit as a sensitizer for many photochemical reactions. We have therefore examined the photochemistry of thioxanthone and would like to report data that confirm the existence of the self-quenching reaction for thioxanthone, but establish its rate as 2.3 ± 0.5 × 10^9 l./(mol sec) rather than the reported 6 × 10^{10} l./(mol sec).

Table I

Sensitizer	k_q (eq 1), l./(mol sec)
p-Methoxyacetophenone[a]	9 × 10^7
m-Methoxyacetophenone[a]	8 × 10^8
Michler's ketone[b]	1 × 10^9
3,4-Methylenedioxyacetophenone[a]	4 × 10^9
Thioxanthone[a]	6 × 10^{10}

[a] Reference 3. [b] Reference 2.

As we reported in an earlier communication,[4] no quenching is observed in the isomerization of 0.1 *M* solutions of *trans*-stilbene in degassed benzene with a thioxanthone concentration of up to 0.05 *M*. The same result has now been obtained in the isomerization of 0.1 *M* dimethyl fumarate, the dimerization of 0.1 *M* indene, and the dimerization of 0.1 *M* methyl indene-2-carboxylate, when sensitized by 0.001–0.1 *M* thioxanthone. On the other hand, Chapman[3] reports strong quenching in the thioxanthone-sensitized rearrangement of 0.1 *M* 4,4-dimethylcyclohexenone in *tert*-butyl alcohol, and we now report a similar strong quenching by thioxanthone on the dimerization of 1.22 *M* 2-cyclopentenone. At first glance it might appear that the enone triplet state and the thioxanthone ground state are involved in the quenching reaction (eq 2) since the quenching is observed only with enones. However, reaction 2 is ruled out by a wavelength experiment. When benzene solutions of 1.22 *M* cyclopentenone and 5 × 10^{-3} *M* thioxanthone are irradiated at 365 nm (absorption by thioxanthone), strong quenching is observed. When 313- or 335-nm radiation is used (absorption by cyclopentenone), no quenching is seen. This experiment clearly shows that the quenching reaction involves the thioxanthone triplet and the thioxanthone ground state (eq 1). These results are plotted in Figure 1. We believe that the reason quenching by thioxanthone (E_t = 65 kcal/mol)[5] has been observed with enones but not with stilbene (0.1 *M*, E_t = 50 kcal/mol),[6] indene (0.1 *M*, E_t = 59 kcal/mol),[7] or dimethyl fumarate (0.1 *M*, E_t = 61 kcal/mol)[6] is that energy transfer from thioxanthone to these low-energy acceptors is diffusion controlled, but is considerably less than diffusion controlled to the enone systems. Our observations are in agreement with de Mayo's estimate for the triplet energy of the enone chromophore (E_t = 70 kcal/mol)[8] and with his observation that energy transfer from benzophenone (E_t = 68.5 kcal/mol)[5] to cyclopentenone is much slower than diffusion con-



(2)

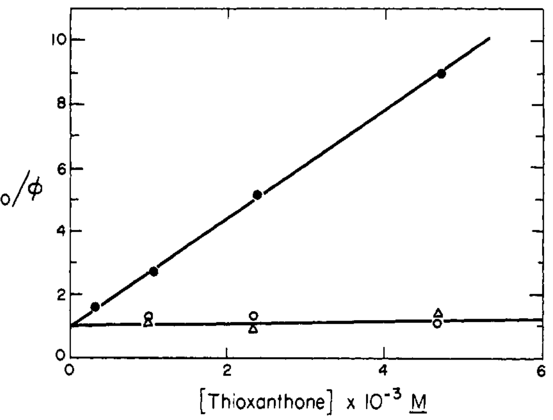


Figure 1. Quenching of cyclopentenone dimerization by thioxanthone: irradiation at ●, 365 nm; ○, 313 nm; and △, 335 nm.

---

(1) C. D. DeBoer, N. J. Turro, and G. S. Hammond, *Org. Syn.*, **47**, 64 (1967).

(2) T. H. Koch and A. H. Jones, *J. Amer. Chem. Soc.*, **92**, 7503 (1970).

(3) O. L. Chapman and G. Wampfler, *ibid.*, **91**, 5390 (1969).

(4) A. G. Schultz, C. D. DeBoer, W. G. Herkstroeter, and R. H. Schlessinger, *ibid.*, **92**, 6088 (1970).

(5) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley, New York, N. Y., 1966, p 298.

(6) G. S. Hammond, J. Saltiel, A. A. Lamolo, N. J. Turro, J. S. Bradshow, D. O. Cowan, R. C. Counsell, V. Vogt, and J. C. Dalton, *J. Amer. Chem. Soc.*, **86**, 3197 (1964).

(7) R. C. Heckman, *J. Mol. Spectrosc.*, **2**, 27 (1958).

(8) P. de Mayo, *Accounts Chem. Res.*, **4**, 41 (1971).