ston-Salem, N. C., for a generous initial sample of solanesol. Our simplified procedure for the isolation of solanesol from tobacco will be described later.

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MERCK, SHARP & DOHME
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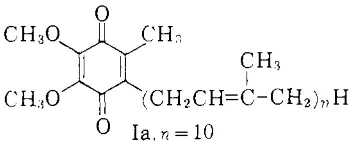
RECEIVED JULY 31, 1959

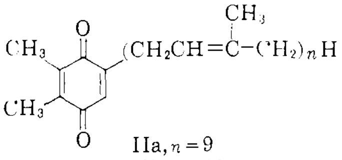
COENZYME Q. X. SYNTHESIS OF COENZYME Q_9, 2,3-DIMETHYL-5-SOLANESYLBENZOQUINONE (*Q-254*), AND A VITAMIN K ANALOG

Sir:

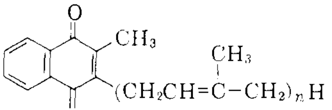
A polyisoprenoid alcohol, solanesol, was isolated from tobacco and evidence was presented indicating that it was composed of 10 isoprenoid units.[1] We obtained a sample of solanesol through the generosity of Dr. R. L. Rowland and Dr. M. Senkus[2] to condense with 2,3-dimethoxy-5-methylhydroquinone, because the reaction could be expected to give synthetic coenzyme Q_{10} (Ia).[3,4,5,6] The resulting 2,3-dimethoxy-5-methyl-6-solanesylbenzoquinone, m.p. 42–43.5°, $\lambda_{max}^{isooctane}$ 271 mμ ($E_{1cm}^{1\%}$ 175). (*Anal.* Found: C, 81.06; H, 10.47) was different from coenzyme Q_{10}, but proved to be indistinguishable from coenzyme Q_9 (Ib)[3] with respect to m.p., R_f, ultraviolet, and infrared data. The structure of solanesol was reinvestigated[7] and it was found to be composed of nine isoprenoid units rather than ten.



Ia, $n = 10$
Ib, $n = 9$



IIa, $n = 9$
IIb, $n = 10$



IIIa, $n = 7$
IIIb, $n = 9$

A quinone (Q-254) has been isolated[8] from alfalfa and has been shown to be 2,3-dimethylbenzoquinone with a substituent in the 5-position composed of 9-isoprenoid units (IIa).[9] Kofler and co-workers[10] have proposed structure IIb which has a 10-isoprenoid unit side chain for a plant quinone believed to be identical with "Q-254." The structure having the 9-isoprenoid unit side chain has been confirmed by synthesis. 2,3-Dimethylhydroquinone was condensed with solanesol in the presence of boron trifluoride etherate, and the resulting hydroquinone was oxidized yielding 2,3-dimethyl-5-solanesylbenzoquinone (IIa), m.p. 43.5–45°, $\lambda_{max}^{isooctane}$ 253 mμ ($E_{1cm}^{1\%}$ 239) and 261 mμ ($E_{1cm}^{1\%}$ 222) (*Anal.* Found: C, 84.87; H, 10.63). This compound is identical with "Q-254" with respect to m.p., R_f, ultraviolet, infrared and nuclear magnetic resonance data.

Vitamin K_2 recently has been shown to have the formula IIIa.[11] We have now synthesized the corresponding naphthoquinone in which the side chain contains nine isoprenoid units (IIIb). 2-Methylnaphthohydroquinone was condensed with solanesol in the presence of boron trifluoride etherate. Oxidation of the product yielded 2-methyl-3-solanesylnaphthoquinone (IIIb), m.p. 60–61°, $\lambda_{max}^{isooctane}$ 243, 248, 260, 269 and 322 mμ ($E_{1cm}^{1\%}$ 218, 232, 212, 210 and 38 resp.) (*Anal.* Found: C, 85.01; H, 10.39).

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[1] R. L. Rowland, P. H. Latimer and J. A. Giles, THIS JOURNAL, **78**, 4680 (1956).

[2] R. J. Reynolds Tobacco Co., Winston-Salem, North Carolina.

[3] R. L. Lester, F. L. Crane and Y. Hatefi, THIS JOURNAL, **80**, 4751 (1958).

[4] D. E. Wolf, C. H. Hoffman, N. R. Trenner, B. H. Arison, C. H. Shunk, B. O. Linn, J. F. McPherson and K. Folkers, *ibid.*, **80**, 4752 (1958).

[5] C. H. Shunk, B. O. Linn, E. L. Wong, P. E. Wittreich, F. M. Robinson and K. Folkers, *ibid.*, **80**, 4753 (1958).

[6] R. A. Morton, U. Gloor, O. Schindler, G. M. Wilson, L. H. Chopard-dit-Jean, F. W. Hemming, O. Isler, W. M. F. Leat, J. F. Pennock, R. Ruegg, U. Schwieter and O. Wiss, *Helv. Chim. Acta*, **41**, 2343 (1958).

[7] R. E. Erickson, C. H. Shunk, N. R. Trenner, B. H. Arison and K. Folkers, THIS JOURNAL, **81**, 4999 (1959).

[8] F. L. Crane and R. L. Lester, *Plant Physiol.*, **33** (Suppl.), VII (1958).

[9] N. R. Trenner, B. H. Arison, R. E. Erickson, C. H. Shunk, D. E. Wolf and K. Folkers, THIS JOURNAL, **81**, 2026 (1959).

[10] M. Kofler, A. Langemann, R. Ruegg, L. H. Chopard-dit-Jean, R. Rayroud and O. Isler, *Helv. Chim. Acta*, **42**, 1283 (1959).

[11] O. Isler, R. Ruegg, L. H. Chopard-dit-Jean, A. Winterstein and O. Wiss, *ibid.*, **41**, 786 (1958).

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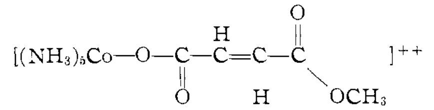
RECEIVED JULY 31, 1959

ACTIVATION OF BRIDGING GROUPS IN ELECTRON TRANSFER. II. THE POSITION OF BOND-BREAKING IN ESTER HYDROLYSIS[1]

Sir:

It has been shown that when certain half-esters function as bridging groups for electron transfer, ester hydrolysis accompanies electron transfer. The point of bond scission in these hydrolyses is a matter of interest, and forms the subject of this communication. The reaction of Cr^{++} with



$$\left[(\mathrm{NH_3})_5\mathrm{Co{-}O{-}}\underset{\substack{\| \\ \mathrm{O}}}{\mathrm{C}}{-}\overset{\mathrm{H}}{\mathrm{C}}{=}\underset{\mathrm{H}}{\mathrm{C}}{-}\overset{\substack{\mathrm{O} \\ \|}}{\mathrm{C}}{\diagdown}\mathrm{OCH_3}\right]^{++}$$

(the ligand is the methyl half ester of fumaric acid, containing oxygen of normal isotope composition) was carried out in aqueous solution 8.5-fold enriched in O^{18} and containing 0.3 *M* $HClO_4$. The fumaric acid was removed as described earlier,[2] and after purification was heated with $Hg(CN)_2$ and $HgCl_2$[3] to convert oxygen to CO_2. The CO_2 was found to be enriched in O^{18} by only a factor of 1.048 above that of a sample derived from acid of normal isotopic composition. Thus it appears

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[1] Supported by the A.E.C. under Contract AT(11-1-)-378.

[2] R. T. M. Fraser, D. K. Sebera and H. Taube, THIS JOURNAL, **81**, 2906 (1959).

[3] M. Anbar and S. Guttmann, private communication.

that the bulk of the reaction occurs with methyl-oxygen bond scission, and the carboxyl carbon-oxygen bond breaks only in 2–3% of the events.

When V^{++} is used as the reducing agent, the procedure for separating the fumaric acid is much simpler than with Cr^{++}; the organic acid can be extracted directly from the reaction mixture. Complete hydrolysis of the ester again accompanies electron transfer. The tracer experiment shows that the CH$_3$-O bond breaks in 95% of the events. With the same reducing agent, but with the methyl maleate half-ester as ligand, bond rupture occurs at the CH$_3$-O position in 97–98% of the hydrolysis events.

When the phenyl fumarate half-ester is the ligand and V^{++} is the reducing agent, complete hydrolysis of the ester also accompanies electron transfer. In this system, the isotopic compositions of both the phenol and the fumaric acid were determined. The results of a series of experiments are summarized.

Acidity of the solution, *M*	1	0.50	0.25	0.05
Fraction of phenol enriched	0.071	.094	.105	.118
Fraction of fumaric acid enriched[a]	0.925	.898	.884	.878

[a] As containing one oxygen derived from the solvent.

The isotope balance is good so that the fractions reported can be taken as indicating the fractions of bond rupture at the two positions. It is evident that the course of the reactions can be altered when an alcohol radical such as C$_6$H$_5$, which is reluctant to accept substitution is used. It is perhaps even more remarkable that a substantial fraction of the bond breaking occurs at the C$_6$H$_5$-O position. The results incidentally show that no exchange of the carboxyl oxygen with the solvent accompanies this type of hydrolysis reaction, in contrast to the behavior demonstrated for a number of other ester hydrolyses.[4]

(4) M. L. Bender, THIS JOURNAL, **73**, 1626 (1951); references to other work cited by M. L. Bender, R. D. Ginger and J. P. Unik, *ibid.*, **80**, 1044 (1958).

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RECEIVED AUGUST 5, 1959

CHARGE TRANSFER LUMINESCENCE OF A RUTHENIUM(II) CHELATE

Sir:

We would like to report the first example of luminescence resulting from a charge transfer transition in the transition metal chelate tris-2,2'-bipyridineruthenium(II). The luminescence of chelates has, in general, been studied as a function of electronic transitions within the ligand itself except for a few isolated cases as for the rare earth chelates with energy transfer and luminescence from f–f transitions[1,2] and for luminescence characteristic of copper(II) in mixtures of copper(II) and aminoanthraquinones,[3] as pointed out by Kasha and McGlynn.[4]

The absorption and fluorescence of tris-5-methyl-1,10-phenanthroline ruthenium chelate have been reported and utilized for a microdetermination of ruthenium[5] although the electronic transition involved has not been discussed. The luminescence shown in Fig. 1 was obtained from a 10^{-4} solution of tris-2,2'-bipyridineruthenium(II) chloride at 77°K. The line-like character of the luminescence is reminiscent of the f–f emission in the rare earth chelates. However, it is a completely different phenomenon produced by an allowed transition whose mean lifetime is less than 10^{-4} sec.[6] As shown by the absorption spectra in Fig. 1 there is no analogous allowed absorption band at the wave length of the luminescence.

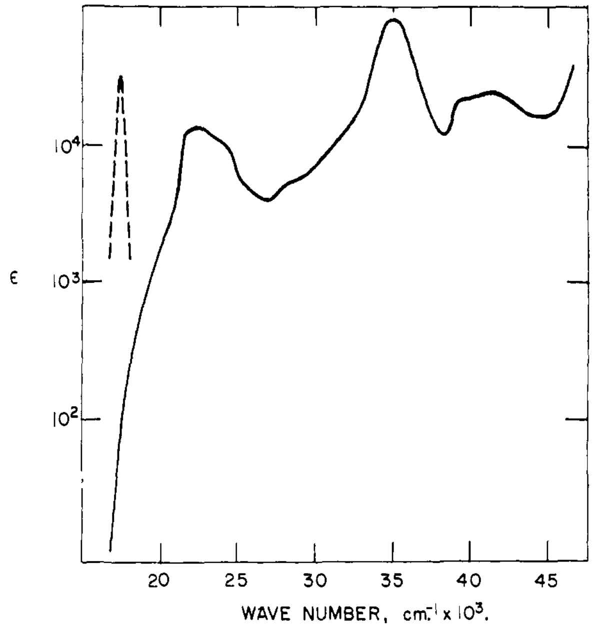

Fig. 1.—Tris-2,2'-bipyridineruthenium(II) chloride: ——— absorption spectra; --------- luminescence spectra (plotted on an arbitrary intensity scale).

We have explained our data in this manner. The broad absorption band between 17,000 and 27,000 cm.$^{-1}$ may be due to a charge transfer absorption ($\epsilon > 10^4$). That is, the d electron from the ruthenium atom may be excited to an antibonding orbital of the bipyridine molecule (d → pi*). Thus we may have a very broad absorption band due to excitation to various vibrationally excited levels of the pi* electronic state and yet have a single emission from the lowest vibrational level of the excited state to the ground d orbital. This may be represented pictorially as shown in Fig. 2.

As predicted there should also be an absorption band from the d orbital to the second antibonding pi orbital. This band was found experimentally to have $\epsilon_{\text{max.}}$ at 41250 cm.$^{-1}$ as shown in Fig. 1. The remaining band with $\epsilon_{\text{max.}}$ at 35000 cm.$^{-1}$ is of course the pi → pi* transition of bipyridine. Ex-

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(1) S. I. Weissman, *J. Chem. Phys.*, **10**, 214 (1942).

(2) G. A. Crosby and M. Kasha, *Spectrochim. Acta*, **10**, 377 (1958).

(3) A. V. Karyakin and Ya. I. Kalenichenko, *Doklady Akad. Nauk S.S.S.R.*, **66**, 191 (1949).

(4) M. Kasha and S. P. McGlynn, *Ann. Rev. Chem.*, **7**, 403 (1956).

(5) H. Veening, Ph.D. Thesis, Purdue University, 1958. Submitted to *Analytical Chemistry*.

(6) The lifetime estimate was kindly provided by Dr. M. Kasha at the Florida State University.