Methyl *p*-Ethylbenzenesulfonate.—A solution of 53 g. of *p*-ethylbenzenesulfonyl chloride in 63.5 ml. of methanol was placed in a reaction flask and cooled to 20° by immersion of the flask in a salt-ice-bath. The solution was stirred continuously while a solution of 40 g. of sodium hydroxide in 30 ml. of water was added slowly. The temperature was held at 23–25° during the addition. The reaction mixture was cooled to 0° and let stand for two hours. Sufficient water was added to dissolve the precipitated sodium chloride. The ester layer was decanted, washed with two 20-ml. portions of water and then with 40 ml. of a 5% sodium carbonate solution, dried over anhydrous sodium sulfate, and distilled to give 31.4 g. or 61% of the theoretical amount of methyl *p*-ethylbenzenesulfonate, b.p. 125–135° at 2 mm. Refractionation through a column packed with helices gave a sample, b.p. 128° at 2 mm., $n^{20}D$ 1.5181, sp. gr. 20/20 1.193, which was used for analysis.

Anal. Calcd. for $C_9H_{12}O_3S$: S, 16.0. Found: S, 15.85.

Ethyl *p*-Ethylbenzenesulfonate.—This ester was prepared using the procedure described for the methyl ester except that the reaction was run at 10°. The yield of ester b.p. 120–137° at 2 mm. was 20.9 g. or 67% of the theoretical amount. Refractionation through a column packed with helices gave a sample b.p. 142–150° at 4 mm., $n^{20}D$ 1.5150, sp. gr. 20/20 1.178, which was used for analysis.

Anal. Calcd. for $C_{10}H_{14}O_3S$: S, 14.95. Found: S, 14.70.

***n*-Butyl *p*-Ethylbenzenesulfonate.**—A mixture of 30 g. of *p*-ethylbenzenesulfonyl chloride and 18 ml. of *n*-butanol was cooled to 5°. To this solution, 23 ml. of pyridine was added over a three-hour period while maintaining the reaction mixture at a temperature of 8–18°. The reaction mixture was cooled to 3° and treated with sufficient dil. hydrochloric acid to neutralize the pyridine. The ester layer was separated and taken up in ether. The ether solution was washed with water and with 5% sodium carbonate and dried over anhydrous sodium sulfate. On fractionation 25.3 g. or 71.6% of the theoretical amount of *n*-butyl *p*-ethylbenzenesulfonate, b.p. 148–150° at 2 mm., was obtained. Refractionation through a column packed with helices gave a sample, b.p. 159° at 4 mm., $n^{20}D$ 1.5051; sp. gr. 20/20 1.114.

Anal. Calcd. for $C_{12}H_{18}O_3S$: S, 13.22. Found: S, 13.38.

Ultraviolet Absorption Data.—Ultraviolet absorption measurements were made with a Beckman DU photoelectric spectrophotometer using 1.00-cm. silica cells and hydrogen and tungsten discharge lamps as light sources. In all measurements 95% ethanol was used as a solvent. The esters and chloride showed an absorption maximum at 264 ± 2 mμ.

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The Charge Transfer Reaction between Molybdo- and Molybdioctacyanides[1]

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The high coördination number and the apparently very close structural similarity of the octacyanides of Mo(IV) and Mo(V) as well as, to a lesser extent, their high net charges lends interest to the charge transfer process between these two complexes. In particular, this case should be a significant indication of the validity of Libby's proposal[2] that the Franck–Condon principle is of primary importance in determining the rates of oxidation–reduction reactions in solution.

$K_4Mo(CN)_8$ and $K_3Mo(CN)_8$ were prepared by the method described by Willard and Thielke.[3] The same compounds containing 66-hr. Mo^{99} were made from MoO_3 irradiated in the Brookhaven reactor. The purity of the $K_4Mo(CN)_8$ was found by titration with $KMnO_4$ to be 99.9%. Decomposition of $K_3Mo(CN)_8$ to $K_4Mo(CN)_8$—a photo-induced reaction—was found to be negligible in the time of the runs.

Three different separations of the two complexes were developed: (1) Several organic solvents miscible with water were found to precipitate $Mo(CN)_8^{-4}$ while leaving $Mo(CN)_8^{-3}$ in solution. This method is effective at concentrations greater than $\sim 10^{-3} f$. In practice separations were carried out by adding five volumes of absolute alcohol to one volume of reactant solution. (2) Cd(II) gives good precipitates with $Mo(CN)_8^{-4}$ at concentrations down to $\sim 10^{-3} f$ while leaving $Mo(CN)_8^{-3}$ in solution. (3) Tetraphenylarsonium chloride was found to give filterable precipitates with concentrations of $Mo(CN)_8^{-3}$ down to 10^{-4}–$10^{-5} f$. In basic solution $Mo(CN)_8^{-4}$ gave no precipitate, while in acid solution the concentration of $Mo(CN)_8^{-4}$ had to be kept below $\sim 10^{-3} f$ to prevent precipitation.

After separation by one of the above techniques, the second species was precipitated by a suitable method. Following a one-day wait to allow equilibration of the daughter Tc^{99m} both fractions were counted.

Using the above techniques over a wide range of *p*H and of anions present in solution, all experiments showed complete exchange, within the experimental error of 10%, in the approximately 5 seconds required for separation. Table I gives the conditions under which some typical experiments were carried out. All runs were made in very dim light at a temperature of 2 ± 1°.

The exchange between one of the species freshly precipitated by the separating agent and the other species was also measured in a series of runs analogous to those in Table I. In all cases a definite but incomplete heterogeneous exchange was found.

The possibility exists that in the homogeneous reaction the complete exchange found is induced by the separation.[4] The likelihood of this is decreased by the use of three distinct separation methods (although in this connection it would have been advantageous if a rapid non-precipitation technique could also have been used). It may be concluded that the charge exchange between $Mo(CN)_8^{-3}$ and $Mo(CN)_8^{-4}$ in aqueous solution is probably an extremely rapid process with a rate constant, if a second-order rate law is obeyed, greater than 10^3 f^{-1} sec.$^{-1}$ at 2°.

It has been shown that the cyanides attached to the central Mo do not exchange.[5] This fact in conjunction with the high degree of coördination involved makes it very unlikely that this charge transfer reaction proceeds by a radical or ion-exchange mechanism. It seems probable then that a true homogeneous electron transfer process is involved here.

Magnetic susceptibility measurements show that $K_4Mo(CN)_8$ is diamagnetic while $K_3Mo(CN)_8$ has a paramagnetism corresponding to one unpaired

(1) Research carried out under the auspices of the U. S. Atomic Energy Commission.

(2) W. F. Libby, Symposium on Electron Transfer and Isotopic Reactions, *J. Phys. Chem.*, **56**, 863 (1952).

(3) H. H. Willard and R. C. Thielke, THIS JOURNAL, **57**, 2609 (1935).

(4) A. C. Wahl and N. Bonner, "Radioactivity Applied to Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1951, p. 16.

(5) A. W. Adamson, J. P. Welker and M. Volpe, THIS JOURNAL, **72**, 4033 (1950).

TABLE I

TYPICAL CONDITIONS FOR $Mo(CN)_8^{-3}$–$Mo(CN)_8^{-4}$ EXCHANGE

Mo(IV), *f*	Mo(V), *f*	Other species, *f*	*p*H	Separation agent	Extent of exchange, %
5.0×10^{-2}	1.5×10^{-2a}	ClO_4^-, 2×10^{-2}; NH_4^+, 1×10^{-2}	2	C_2H_5OH	94
1.7×10^{-3}	1.2×10^{-4a}	ClO_4^-, 4×10^{-4}; NH_4^+, 1×10^{-4}	4–5	$Cd(NO_3)_2$ 0.1*f*	100
5.0×10^{-5a}	1.5×10^{-4}	Cl^-, 7×10^{-4}; NH_4^+, 3×10^{-3}	10–11	$(C_6H_5)_4AsCl$ 0.2*f*	100
9.6×10^{-4a}	1.1×10^{-3}	Cl^-, 1×10^{-2}; NH_4^+, 1×10^{-3}	1–2	$(C_6H_5)_4AsCl$ 0.2*f*	106
5.0×10^{-5}	4.0×10^{-5a}	NO_3^-, 1×10^{-4}; NH_4^+, 3×10^{-5}	6–8	$(C_6H_5)_4AsCl$ 0.2*f*	116

[a] Denotes initially active species.

electron.[6] This implies that both complexes have d^4sp^3 binding and should thus have a very similar configuration and internuclear spacing. It follows that the Franck–Condon principle should not impose any considerable barrier to electron transfer —a prediction which is in accord with the experimental findings. The results, furthermore fit well into an empirical correlation proposed by Adamson,[7] according to which exchange is rapid between species both having a low magnetic susceptibility.

The author greatly appreciates the helpful discussions of Dr. R. W. Dodson who first pointed out to him the interest which might be attached to this research. The advice of Dr. Joan Welker on the method of preparation and the kindness of Dr. A. W. Adamson in supplying the author with a sample of $K_4Mo(CN)_8 \cdot 2H_2O$ are gratefully acknowledged.

(6) P. W. Selwood, "Magnetochemistry," Interscience Publishers, Inc., New York, N. Y., 1943, p. 150.

(7) A. W. Adamson, *J. Phys. Chem.*, in press (1952).

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Synthetic C^{14}-"Squalene": Concerning its Incorporation into Cholesterol by Liver[1]

BY G. M. TOMKINS,[2] I. L. CHAIKOFF, W. G. DAUBEN, H. L. BRADLOW AND P. A. SRERE

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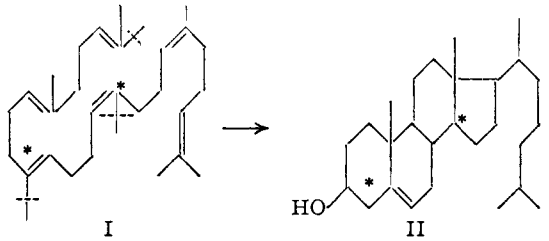
In 1926 and again in 1937, Channon[3] reported that the feeding of the hydrocarbon squalene (I) to rats resulted in an increase in the cholesterol (II) contents of their livers. In 1934, Robinson[4] suggested that by the following cyclization of the dihydrotriterpene, this compound might serve as a direct precursor of cholesterol.



I II

Subsequent work utilizing labeled acetate[5] has yielded results which can readily be interpreted in terms of this hypothesis[6] and, indeed, recently Langdon and Bloch[7] demonstrated the conversion of labeled squalene to this sterol.

Independently, we had undertaken[8] to study this conversion and should like to report our results employing specifically labeled, synthetic "squalene."[9] The metabolic fate of this compound was studied both *in vitro* and *in vivo*. The former type of experiment was conducted in two distinct fashions, (1) the compound, dispersed in saline with the aid of Tween 80, was incubated with liver slices and (2) liver slices of animals previously injected with the labeled material were incubated. In the *in vivo* experiment, the "squalene" was introduced by stomach tube into fasted rats. The results of these experiments are given in Tables I, II and III.

TABLE I

Liver slices incubated in the presence of labeled substrate for 3 hours at 37.5°

Expt.	Wt. of slices, g.	Contents of flask: Substrate	μM.	C^{14}, c.p.m.	Per cent. of added C^{14} recovered as CO_2	Cholesterol
I	1	Acetate-1-C^{14}	5	6.85×10^5	31.0	0.82
	1	Squalene-C^{14}		7.5×10^5	0.40	0
II	1	Acetate-1-C^{14}	5	6.85×10^5	36.0	0.68
	1	Squalene-C^{14}		7.5×10^5	0.62	0
III	1	Acetate-1-C^{14}	5	6.85×10^5	34.0	0.62
	1	Squalene-C^{14}		7.5×10^5	0.46	0

TABLE II

The labeled substrate was injected into the portal vein at time of sacrifice, and liver slices were incubated for 3 hours at 37.5°

Activity injected per 2 g. of liver, c.p.m.	Weight of liver slices per flask, g.	Per cent. of added C^{14} recovered as CO_2	Cholesterol
5.0×10^5	2	0.11	0.0
	2	.20	.0

TABLE III

The labeled substrate was administered enterally

Animal	Total activity administered, c.p.m.	Total activity in liver at end of 24 hr., c.p.m.	Per cent. C^{14} administered recovered as cholesterol
1	9.0×10^5	2.4×10^4	0.0
2	1.7×10^6	5.7×10^4	.0

(1) Aided by a grant from the U. S. Public Health Service and the Life Insurance Medical Research Fund.

(2) Life Insurance Medical Research Fellow.

(3) H. J. Channon, *Biochem. J.*, **20**, 400 (1926); H. J. Channon and B. R. Tristam, *ibid.*, **31**, 738 (1937).

(4) R. Robinson, *J. Soc. Chem. Ind.*, **53**, 1062 (1934).

(5) H. N. Little and K. Bloch, *J. Biol. Chem.*, **183**, 33 (1950), and earlier papers.

(6) P. Srere (Dissertation, Univ. of California, 1951), in this Laboratory, has demonstrated that livers from animals kept for 30 days on a 1% squalene diet, show a decreased ability to incorporate C^{14}-labeled acetate into cholesterol but not into carbon dioxide. Such a result is compatible with the concept that an intermediate metabolic pool in the conversion acetate to cholesterol has been diluted or that squalene might act as a specific precursor of the sterol.

(7) R. G. Langdon and K. Bloch, THIS JOURNAL, **74**, 1869 (1952).

(8) "Ciba Foundation Conference on Isotopes in Biochemistry," J. and A. Churchill, Ltd., London, W. 1, England, p. 24 ff.

(9) The term "squalene" is used to indicate that the synthetic product is a dihydrotriterpene with six double bonds and is a mixture of double bond isomers (see W. G. Dauben and H. L. Bradlow, THIS JOURNAL, **74**, in press (1952)).