TABLE V

T = 65°C., SOLVENT ISOÖCTANE

Hydrocarbon	Mole, %	$(k_2/k_1)_{exp.}$
Pentyne-1	10.51	4.61
Pentyne-1	7.88	5.94
Pentyne-1	5.26	7.30
Pentyne-1	2.63	9.26
Pentyne-1; k_2/k_1 extrapolated to 0 mole % = 13.7		
Hexyne-1	10.45	6.00
Hexyne-1	7.84	7.00
Hexyne-1	5.24	8.86
Hexyne-1	2.62	12.50
Hexyne-1; k_2/k_1 extrapolated to 0 mole % = 17.5		

TABLE VI

T = 65°C., SOLVENT ISOÖCTANE

Hydrocarbon	k_2/k_1	k_3/k_2	k_5/k_1	k_5'/k_1
Pentyne-1	13.7	1.2	16.3	8.1
Hexyne-1	17.5	0.97	17.0	8.5

compare reasonably with the k_2/k_1 value determined for methylacetylene, namely, 10.85, and thus it appears that the rate of addition of methyl radicals to an acetylene of the type CH≡C—R is, at least approximately, independent of the length of the group R.

It is interesting to compare the rate of abstraction of hydrogen atoms from the CH_2 group α to C≡C triple bond with the rate of abstraction from the same group α to C═C double bond. The results arrived at from the study of reactions of pentyne and hexyne lead to values 8.1 and 8.5, respectively, for the ratio k_5'/k_1 (k_5' represents the rate constant of hydrogen abstraction reaction per active hydrogen, *i.e.*, $k_5/2$ for the discussed hydrocarbons). On the other hand, the work of Buckley and Szwarc[12] demonstrated that the corresponding values of k_5'/k_1 for butene-1, pentene-1, heptene-1, decene-1 and hexadecene-1 are 3.3, 4.1, 6.3, 6.4 and 6.4, respectively. It appears, therefore, that the rate of abstraction of a hydrogen atom from a CH_2 group adjacent to a C≡C triple bond is slightly higher than the corresponding rate for a reaction involving a CH_2 group adjacent to a C═C double bond. This point will be discussed further in a forthcoming publication.

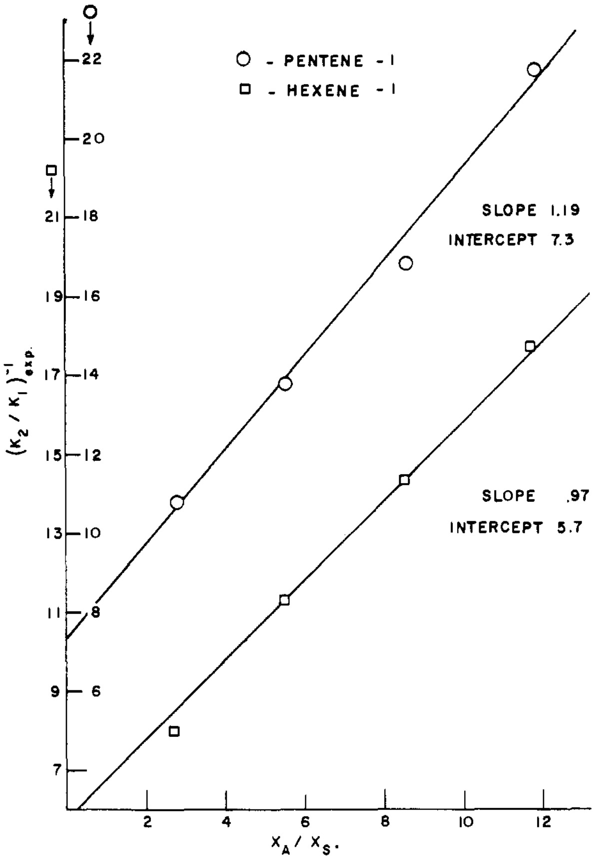

Fig. 3.

In conclusion we wish to thank the National Science Foundation for their support of this investigation.

SYRACUSE, N. Y.

[CONTRIBUTION FROM BAKER LABORATORY OF CHEMISTRY, CORNELL UNIVERSITY]

Photochemical Exchange of Water between $Cr(H_2O)_6^{+3}$ and Solvent[1]

BY ROBERT A. PLANE AND JOHN P. HUNT

RECEIVED DECEMBER 3, 1956

Studies have been made on the rate of the reaction $Cr(H_2O)_6^{+3} + 6H_2O^{18} \rightarrow Cr(H_2O^{18})_6^{+3} + 6H_2O$ in the presence of light of various wave lengths. Quantum yields have been obtained for the three $Cr(H_2O)_6^{+3}$ absorption bands (2610, 4080, 5740 Å.) at three temperatures (0, 10, 27°). At 27°, the quantum yields for all bands are of the order of magnitude 10^{-2}, and decrease with decreasing temperature. Solutions of $Cr(H_2O)_6(ClO_4)_3$ were carefully checked for fluorescence which was found to be absent even at −196° in glasses prepared by dissolving $Cr(H_2O)_6(ClO_4)_3$ in isopropyl alcohol. In order to account for the low quantum yields and absence of fluorescence, it seems most likely that the electronically excited chromic species converts to the ground state by radiationless transitions to high vibrational states of the ground electronic level. Because of the large temperature dependence of the photochemical reaction, it appears more probable that reaction occurs from an excited electronic state rather than from an excited vibrational state. However, such an interpretation seems to demand that during deactivation, some of the chromic species must pass through a spin forbidden (doublet) state.

For many years it has been known that some substitution reactions of complex ions are hastened by light. Most such reactions seem to be particularly sensitive to ultraviolet radiation, and the mechanisms which have been proposed usually involve an electron transfer followed by rapid substitution. For example, for a series of complex ions of the type $[Co(NH_3)_5X]^{++}$ (in which X is F^-, Cl^-, Br^- or I^-)

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[1] Presented at 128th National Meeting of the American Chemical Society, Minneapolis, Minnesota, 1955.

Linhard and Weigel have proposed that the photodecomposition is due to an electron transfer from X^- to the Co atom forming the cobaltous complex ion which rapidly decomposes.[2] Recently, several authors have interpreted the ultraviolet and visible absorption spectra of a number of complex ions including $Cr(H_2O)_6^{+3}$.[3] The spectrum of $Cr(H_2O)_6^{+3}$ in solution was measured by the present authors using a calibrated Beckman DU spectrophotometer, and is reproduced in Fig. 1. The spectrum in Fig. 1 was obtained from a 0.04 *M* solution of $Cr(H_2O)_6(ClO_4)_3$ which contained 0.1 *M* $HClO_4$. The absorption follows Beer's law, is unaffected by addition of perchloric acid or sodium perchlorate, and is essentially temperature independent. At very short wave lengths (below 2400 Å.) there is a strong absorption which has been attributed to an electron transfer. However, the three weak absorption bands at longer wave lengths are assigned to forbidden electronic transitions within the 3d subshell of the chromium atom.[3] The present work was undertaken to determine whether irradiation of the three weak absorption bands of $Cr(H_2O)_6^{+3}$ might hasten its substitution reactions which normally are quite slow.[4]

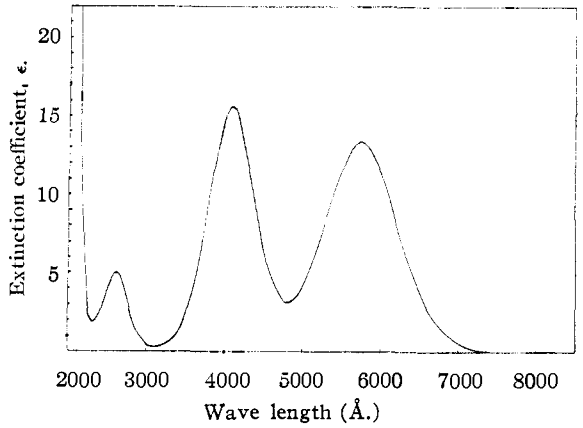

Fig. 1.—Absorption spectrum $Cr(H_2O)_6^{+++}$.

The particular substitution reaction chosen for study was the isotope exchange reaction

$$Cr(H_2O)_6^{+3} + 6H_2O^{18} \longrightarrow Cr(H_2O^{18})_6^{+3} + 6H_2O$$

It was chosen because considerable data already exist for the "dark" reaction,[4] there is no change in spectrum during the course of the reaction, and this reaction should be relatively simple in nature.

Experimental

The general procedure followed involved preparation of a solution of $Cr(ClO_4)_3$ and $HClO_4$ in which the solvent water (but not $Cr(H_2O)_6^{+3}$) was initially enriched in O^{18} by about a factor of 3. A portion of the solution was taken for analysis of the initial O^{18} content of the $Cr(H_2O)_6^{+3}$ and the remainder was then irradiated for a number of hours. After irradiation, the solution was again sampled and the remainder allowed to stand until isotopic equilibrium had been attained and then sampled again. The rate of the "dark" reaction was obtained either from the previous data,[4] or in some cases from new experiments run parallel with the photoreactions. In all cases, ClO_4^- was the only anion present.

The materials used were prepared by methods described previously,[4] and the sampling procedure was essentially the $Cr(H_2O)_6PO_4$ precipitation and ignition used earlier.[4] The only difference in sampling procedure was that the precipitate was ignited at 160° without the subsequent heating to 750° as done in earlier work. Despite the fact that this lower temperature ignition served to remove but *ca.* $4H_2O/Cr$, the elimination of oxygen exchange between water and phosphate seemed to allow slightly greater reproducibility of results.

For irradiations, a cylindrical cell was used with light filters serving as a cover. The light came from above the cell in a slightly divergent beam which did not strike the walls of the cell. In most experiments, nearly all of the light was absorbed in the solution. In cases where this condition did not obtain, appropriate corrections were applied to the results. During irradiation, solutions were thermostated and were stirred using a magnetic stirrer. Light sources were the General Electric Co. AH-4, AH-5 and 4-watt germicidal lamp. Appropriate Corning filters were used to select wave lengths such that each absorption band could be irradiated separately. The light was monitored during the experiments using a Weston Photronic cell and was found to be constant in intensity during an experiment to ±3%. Quantum fluxes were measured in the reaction cell, before and after a run, using the uranyl oxalate actinometer.[5] For wave lengths longer than 4500 Å., the photochemical experiment was run with one set of filters and the actinometer with another set. Results were then calculated from data supplied by the lamp manufacturer on the relative intensities of various spectral bands and by measuring the transmission of the various filters. This method was checked by direct measurement with a calibrated photronic cell giving good agreement.

Results

The data obtained and results calculated are summarized in Table I.

TABLE I

PHOTOCHEMICAL RESULTS

Range (Å.) irradiated	*t*, °C.	Moles quanta / l.-hr.	Total rate (*M*/hr.) × 10⁴	Dark rate (*M*/hr.) × 10⁴	Quantum yield
2537	−0.35	0.015	0.66	0.14	0.0035 ± 0.0007
2537	10.20	.032	9.4*	4.2*	.016 ± .006
2537	27.53	.016	17.7	13.3	.028 ± .008
2537	27.90	.038	74.4*	65.9*	.022 ± .014
2537	27.53	.012	15.5	13.3	.019 ± .010
2537	27.53	.013	15.7	13.3	.018 ± .009
3500–4800	−0.40	.041	1.32	0.14	.0029 ± .0006
4300–4900	10.50	.0078	1.42	0.91	.007 ± .004
4300–4900	27.62	.0089	16.3	13.5	.031 ± .014
4300–4900	27.93	.0070	15.8	14.2	.023 ± .017
4300–4400	27.65	.0039	14.8	13.5	.033 ± .028
3500–4800	27.65	.043	17.4	13.3	.010 ± .004
3300–3800	27.95	.0090	15.3	14.0	.013 ± .012
3300–7300	28.00	.12	31.5	14.0	.015 ± .003
5400–7300	−0.30	.073	2.18	0.14	.0029 ± .0006
5400–7300	10.50	.013	4.46	0.91	.027 ± .006
5400–7300	27.65	.029	18.8	13.8	.017 ± .004
5400–7300	27.93	.013	18.1	14.0	.032 ± .011

* Concn. of $Cr(ClO_4)_3$ 0.43 *M* and of $HClO_4$ 0.45 *M* instead of concentrations of both 0.10 *M* as in all other experiments.

The data in the table are arranged in three groups corresponding to the three absorption bands of $Cr(H_2O)_6^{+3}$. In all experiments, except the two marked with asterisks, the concentrations of both $Cr(H_2O)_6(ClO_4)_3$ and $HClO_4$ are 0.10 *M*. In the other two $Cr(H_2O)_6(ClO_4)_3$ is 0.43 *M* and $HClO_4$ is 0.45 *M*. In all experiments the rate of the isotope

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[2] M. Linhard and M. Weigel, *Z. anorg. allgem. Chem.*, **266**, 49 (1951).

[3] J. Owen, *Proc. Roy. Soc.* (*London*), **A227**, 183 (1955); L. E. Orgel, *J. Chem. Phys.*, **23**, 1004 (1955); C. K. Jorgensen, *Acta Chem. Scand.*, **9**, 116 (1955).

[4] J. P. Hunt and R. A. Plane, THIS JOURNAL, **76**, 5960 (1954).

[5] W. G. Leighton and G. S. Forbes, *ibid.*, **52**, 3139 (1930); G. S. Forbes and L. J. Heidt, *ibid.*, **56**, 2363 (1934).

exchange reaction is increased slightly on irradiation. The increase corresponds to a quite small quantum yield (molecules reacted per quantum absorbed) which is therefore subject to large experimental error. The probable limits of uncertainty placed on the resultant values of the quantum yield reflect, in most cases, only the ±5% uncertainty in measuring the reaction rates in the presence and absence of radiation. Within the rather large limits of error, there seems to be no dependence of quantum yield on wave length even though different absorption bands are irradiated.

It is seen from Table I that the quantum yield increases with increasing temperature. Although the results are too uncertain to permit accurate evaluation of the activation energy of the photochemical process, they are consistent with a value of 13 kcal. per mole for all three absorption bands. This value is about half of that found for the activation energy of the same reaction in the absence of light (26.7 kcal. per mole).[4]

In order to interpret the photochemical results, solutions of chromic perchlorate were checked for fluorescence.[6] Solutions of chromic concentrations 10^{-4} to 10^{-1} M were irradiated with a mercury arc lamp and observed (using either the eye or a photocell with photomultiplier) at right angles to the incident beam. Each of the three absorption bands was irradiated by using filters between the sample and the light source. When observed through a filter which passed only light of wave length longer than the incident beam, no light was detected even when the light source was very intense such as that obtained from the AH-5. Low temperature studies were made on solutions of $Cr(H_2O)_6(ClO_4)_3$ dissolved in isopropyl alcohol and frozen to a clear glass at liquid nitrogen temperature. Again no fluorescence was detected. It should be noted that the solutions in isopropyl alcohol must have a somewhat different absorption spectrum than the aqueous solutions since they appear green rather than violet.

Discussion

Although the rate of the exchange reaction of $Cr(H_2O)_6^{+3}$ is clearly increased by light absorption, the over-all quantum yield for reaction is quite small. The small yield might result from an extremely large "cage effect," but such an explanation does not seem probable for this particular reaction in which the solvent "cage" is itself a reactant. A more plausible explanation for the small quantum yield might involve a series of events somewhat similar to those described by Zimmerman to account for very small quantum yields (1.4×10^{-5} to 5.4×10^{-2}) for the photodecomposition of permanganate.[7] After excitation of $Cr(H_2O)_6^{+3}$ to any one of the three electronic states corresponding to the three absorption bands, it is expected that rapid radiationless transition should occur to the lowest lying of these, since all three are of the same spin multiplicity (quartet).[8] Since no fluorescence is observed for $Cr(H_2O)_6^{+3}$, it like MnO_4^- might well undergo further radiationless transition to a high vibrational level of the ground electronic state (also a quartet state). The question arises as to whether the exchange reaction occurs during the period of electronic excitation, or during the subsequent vibrational excitation. In the permanganate decomposition, it seems most probable that chemical reaction occurs during vibrational excitation. This conclusion is convincingly supported by the strong dependence of quantum yield on wave length of exciting radiation (5.4×10^{-2} molecules/quantum at 2537 Å. to 1.4×10^{-5} molecules/quantum at 5640 Å.) and the but slight dependence on temperature which increases with increasing wave length (at wave lengths below 4360 Å., no temperature dependence; at 5640 Å., activation energy 4 kcal. per mole).[7] Apparently for irradiation of MnO_4^- at shorter wave lengths, the greater amount of resultant vibrational energy is more efficient in bringing about reaction; at longer wave lengths, some thermal energy must be supplied. However, in the case of $Cr(H_2O)_6^{+3}$, essentially no dependence of quantum yield or activation energy on wave length could be detected. This fact together with the large activation energy observed seems to indicate a marked difference between the photoreactions of MnO_4^- and $Cr(H_2O)_6^{+3}$. In fact, the latter might well undergo reaction while in an electronically excited state.

That electronic excitation should affect reaction rate seems likely in terms of Taube's striking correlation of reaction rate and electronic configuration.[9] Whereas the normal $Cr(H_2O)_6^{+3}$ falls in Taube's class of "inert" complex ions, excitation of the 3d electrons, might be expected to produce a "labile" complex ion.[10] Furthermore, if the exchange reaction occurs while $Cr(H_2O)_6^{+3}$ is in an excited electronic state, the relatively large activation energy can be understood. This energy would correspond to the activation energy for the exchange of the excited species. In the case of other labile complex ion substitution reactions which have been studied by Bjerrum and Poulsen at very low temperatures,[11] activation energies are of the same magnitude. For example, an activation energy of 12.7 kcal./mole was determined for the reaction

$$Fe^{+3} + SCN^- \longrightarrow FeSCN^{+2}$$

However, if the temperature dependence of the present photochemical reaction is due to the excited species requiring activation energy for reaction, it is necessary that the excited species be relatively long lived. An activation energy of 13 kcal./mole would correspond, if the pre-exponential rate factor were the same as for the normal ion (5×10^{14} sec.$^{-1}$),[4] to a mean life for reaction of 6×10^{-6} sec. at 25°. This value should be compared with an estimate of the mean life of the excited state.

From the integrated intensity of absorption bands it is possible to obtain an estimate of the maximum mean lifetime of an excited state.[12]

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[6] The aid of Dr. M. L. Hunt and Dr. A. C. Albrecht is gratefully acknowledged.

[7] G. Zimmerman, *J. Chem. Phys.*, **23**, 825 (1955).

[8] In molecules where fluorescence is observed, it is found to originate only from the lowest state of given multiplicity. *Cf.* M. Kasha, *Disc. Faraday Soc.*, **9**, 14 (1950).

[9] H. Taube, *Chem. Revs.*, **50**, 69 (1952).

[10] L. E. Orgel, *J. Chem. Soc.*, 4756 (1952).

[11] J. Bjerrum and K. G. Poulsen, *Nature*, **169**, 463 (1952).

[12] G. N. Lewis and M. Kasha, THIS JOURNAL, **67**, 994 (1945).

Of the three absorption bands of $Cr(H_2O)_6^{+3}$ only the lowest energy state is considered, since it is assumed that there is quite rapid internal conversion from the higher states. This assumption is consistent both with previous fluorescence studies,[8] and with the observation that in the present case, the quantum yield does not depend upon which absorption band is irradiated. Such an estimate for the lowest energy band is 1.4×10^{-5} sec., which should correspond to the mean life of that state if the only mode for return to the ground state is direct fluorescence. The lack of fluorescence indicates that the actual lifetime of this state is many orders of magnitude less; in fact, too short for any detectable reaction to occur. However, the life time of electronic excitation may actually be much longer than the lifetime of the lowest excited quartet state. According to the spectral assignment of Finkelstein and Van Vleck for solid chrome alum,[13] there is a doublet state which lies fairly close to the lowest excited quartet state. If before conversion to the ground state, some of the excited $Cr(H_2O)_6^{+3}$ passed into such a spin forbidden state of long life time, it could well have sufficient time to undergo the chemical exchange reaction while still electronically excited.

Acknowledgment.—The authors would like to thank their colleagues for many helpful discussions concerning the interpretation of the results. We are especially indebted to Prof. R. Bersohn and Dr. A. C. Albrecht.

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(13) R. Finkelstein and J. H. Van Vleck, *J. Chem. Phys.*, **8**, 790 (1940).

ITHACA, N. Y.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

The Mechanism of Chemisorption: Ethylene and Ethane on Nickel

BY P. W. SELWOOD

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Magnetization–volume isotherms have been obtained for ethylene and for ethane on a commercial nickel-kieselguhr catalyst, and for ethylene on a coprecipitated nickel–silica catalyst. Isotherms have also been obtained for hydrogen on a nickel surface already covered in part with chemisorbed ethylene, and for ethane on a surface already covered with hydrogen. It has been shown that if the d-band of the nickel in these catalysts gains one electron per chemisorbed hydrogen atom, the d-band gains on the average a little over two electrons for each ethylene molecule chemisorbed at room temperature. Admission of ethylene to nickel at higher temperatures is followed by dissociative adsorption or fragmentation. On a coprecipitated catalyst at 100° this fragmentation yields approximately a six-electron transfer per molecule of chemisorbed ethylene. Ethane at room temperature is chemisorbed on a bare nickel surface with somewhat more than a six-electron gain by the nickel per molecule of ethane. Ethane is not chemisorbed on a nickel surface already covered with hydrogen. In these catalyst systems there are three or four times as many nickel sites available to hydrogen as to ethylene, and over six times as many to hydrogen as to ethane. Admission of hydrogen to a nickel surface already covered with ethylene leads both to the formation of ethane and to the chemisorption of hydrogen.

The purpose of this work was to extend the method of magnetization–volume isotherms to ethylene, to ethane, and to certain aspects of the ethylene hydrogenation reaction.[1]

Experimental

All the results reported below were obtained by the induction method previously described.[1] Adsorptions were made and magnetizations were measured at 27° except as otherwise stated.

Two catalyst samples were used. One was Universal Oil Products Company nickel-kieselguhr hydrogenation catalyst, containing 52.8% nickel. This catalyst has an approximate surface area (B.E.T., N_2) of 175 sq. m. per g. The other catalyst was a coprecipitated nickel–silica prepared as described by Van Eyk Van Voorthuisjen and Franzen,[2] and designated by them CLA 5421. This sample contained 37.5% nickel, and had a surface area of about 200 sq. m. per g. Specific magnetization *vs.* temperature for samples similar to these already have been published.[1]

Each sample was reduced in flowing hydrogen before each series of measurements. Reduction was at 360° for 12 hr., followed by evacuation at 10^{-6} mm. for 1 hr. at 360°, and cooling *in vacuo* to 27°.

Hydrogen used for reduction and for adsorption measurements was purified as previously described,[1] as was the helium used for dead-space determination. The ethylene was Phillips Research Grade guaranteed to be 99.9+% pure. The ethane was Mathieson Technical Grade.

The results reported below were obtained on samples weighing 6 to 8 g.

Results

Figure 1 shows automatically recorded changes of magnetization observed when ethylene was flushed over evacuated U. O. P. catalyst, up to atmospheric pressure. The change is negative, that is, in the same direction as that caused by chemisorbed hydrogen on nickel at room temperature. The effect is, however, considerably smaller than that for hydrogen. This accounts for our failure to observe the effect for ethylene at room temperature in our first experiments in which the less sensitive Faraday method was used.[3] We did observe and report the effect of ethylene at higher temperatures, as described below.

It will be seen that there is a fairly large thermal transient caused by the heat of chemisorption. After temperature equilibrium had been reached the sample was evacuated with the result shown, namely, a small positive transient appeared. No permanent change of magnetization was produced by evacuation even though, as will be shown below, over half the ethylene was thus removed. This result merely shows, as is well known, that a large fraction of the ethylene adsorbed on nickel–silica at room temperature is held by van der Waals forces.

Figure 2 shows both magnetization–volume isotherms and, the more familiar, pressure–volume iso-

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(1) P. W. Selwood, THIS JOURNAL, **78**, 3893 (1956).

(2) J. J. B. Van Eyk Van Voorthuisjen and P. Franzen, *Rec. trav. chim.*, **70**, 793 (1951).

(3) P. W. Selwood, S. Adler and T. R. Phillips, THIS JOURNAL, **77**, 1462 (1955).