The Journal of Chemical Physics

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Joseph C. Jungers and Hugh S. Taylor

Citation: The Journal of Chemical Physics **6**, 325 (1938); doi: 10.1063/1.1750260
View online: http://dx.doi.org/10.1063/1.1750260
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/6/6?ver=pdfcov
Published by the AIP Publishing

JUNE, 1938 JOURNAL OF CHEMICAL PHYSICS VOLUME 6

The Mercury Photosensitized Hydrogenation of Ethylene, Ethylene-d_4 and Partially Deuterized Ethylenes

JOSEPH C. JUNGERS[1] AND HUGH S. TAYLOR[2]
Laboratorium voor Physische Scheikunde der Universiteit te Leuven, Belgium

(Received March 10, 1938)

The hydrogenation of ethylene, ethylene-d_4 and partially deuterized ethylene photosensitized by excited mercury to $\lambda = 2537A$ has been studied. It has been found that the rate of hydrogenation of the deutero-compound is more rapid than that of ethylene under comparable conditions. With excess hydrogen, the rate is independent of the ethylene pressure. The data obtained indicate that butane is the important product together with small amounts of ethane relatively more abundant in the case of ethylene-d_4. Negligible amounts of methane are formed. The suggested mechanism involves the reactions $H + C_2H_4 = C_2H_5$ followed by $C_2H_5 + C_2H_5 = C_4H_{10}$ and to a lesser degree, $C_2H_5 + C_2H_5 = C_2H_6 + C_2H_4$. At low hydrogen concentrations, or in absence of hydrogen, a photosensitized polymerization occurs, faster with ethylene than with ethylene-d_4. The slower rate of polymerization of the deutero-compound may be explained on the basis of zero-point energy differences between C_2H_4 and C_2D_4 in their reactions with free radicals to yield more complex radicals.

THE present investigations were begun in the hope that comparative studies of the mercury photosensitized hydrogenation of ethylene and ethylene-d_4 might assist in the solution of problems which remained unsolved in the earlier investigations with ethylene alone.[3] The changes in reaction velocity that result from the use of deutero-compounds in place of hydrogen compounds might serve to indicate the nature of the intermediate stages in the over-all processes observed. The analysis of these stages can be more penetratingly effected now, by reason of our increased knowledge of the kinetic characteristics of the atomic and free radical constituents of systems so produced.[4] The accuracy of such kinetic characteristics can, in turn, be checked by the newer data.

EXPERIMENTAL

Light source

As source of resonance radiation we have employed the Hanovia quartz mercury vapor, rare gas discharge tube, Sc 2537, operating, from a 220 a.c. volt primary, at 5000 volts and 100 milliamperes by means of a suitable transformer. The lamp was a double-U in shape each loop about 15 cm length in leg. Satisfactory operation was secured only when one of the electrodes was kept cooled to constant temperature in a stream of running water. This served to maintain a constant mercury vapor pressure and to prevent clouding of the arc tubing by deposit of mercury on the walls from which radiation entered the reaction system. It was also found that variations in intensity of resonance radiation resulted as the transformer heated up when in use, so that the arc system was operated for a period of time before each experiment so that equilibrium might be established.

Gases

The ethylene used was prepared in two ways (*a*) by the reaction of zinc metal on ethylene dibromide in water solution and (*b*) by the action of sulphuric acid on ethyl alcohol. It was purified by passage through alkali and concentrated sulphuric acid and then submitted to fractional distillation. The results were the same on the two samples.

Deutero-ethylene, kindly placed at our disposal by Professor M. de Hemptinne, was obtained by the action of zinc metal on ethylene dibromide-d_4 obtained by the addition of deuterium bromide to deutero-acetylene. It was purified by the usual method and by a fractional distillation and allowed finally to react with metallic sodium to remove any traces of halogen compounds. The sample contained 95 percent C_2D_4 as determined by measurements of Raman spectra.[5] A partially deuterized ethylene, also studied, was obtained

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[1] Docent, University of Louvain.

[2] Francqui Professor, 1937, University of Louvain.

[3] See, for example, H. S. Taylor and D. G. Hill, J. Am. Chem. Soc. **51**, 2922 (1929).

[4] J. C. Jungers and H. S. Taylor, J. Chem. Phys. **4**, 94 (1936); K. Morikawa, W. S. Benedict and H. S. Taylor, ibid. **5**, 212 (1937).

[5] de Hemptinne, Jungers and Delfosse, J. Chem. Phys., **6**, 319 (1938).

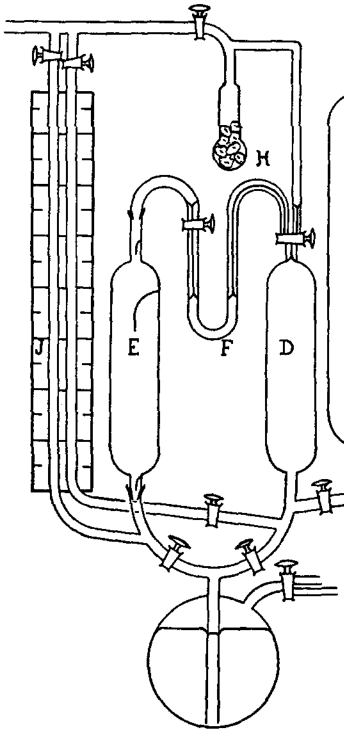

FIG. 1. Apparatus for photosensitized hydrogenation of ethylenes.

by equilibration of ethylene and deuterium oxide on an active nickel catalyst at a temperature of 150°C. The Raman spectra showed that the sample was approximately 50 percent D and contained principally the *cis* and *trans* forms of symmetrical $C_2H_2D_2$, with a little $CH_2=CD_2$ and also small amounts of C_2D_3H and C_2H_3D.

The hydrogen was prepared by electrolysis, freed from oxygen over platinized asbestos and from water vapor in a liquid-air trap and over phosphorus pentoxide. Another sample was further purified by adsorption and desorption from charcoal. No variations in reaction due to method of purification were noted.

Apparatus

The experimental arrangement is shown in Fig. 1. The vessels *A*, *B* and *C* are reservoirs for the gases, *A* and *B* being provided with a side tube in which the ethylenes could be frozen out with liquid air and any noncondensible gases removed by pumping. The reservoir *B* for deutero-ethylene contained metallic sodium. Mixtures of hydrogen and one of the ethylenes in variable concentrations could be introduced into the cylindrical quartz reaction chamber *E* (19 cm × 2.3 cm diameter) after an appropriate mixture had been secured in *D*. Evacuation of the system was effected through the tubes *J* which could also serve as a manometer, The U-tube, *F*, between *D* and *E* could be used to freeze out the condensible gases in liquid air. The uncondensed gas (H_2+CH_4) could then be pumped off by means of *D* and compressed on to the copper oxide tube *H*, the unburnt residue, methane, being then measured in *E*. The condensible gases, after pressure measurement, could be similarly burned in *H* and the residual CO_2 measured in *E* by pressure measurement before and after liquid air was applied to *F*.

In certain experiments a filter of acetic acid solution, 25 percent by volume, was employed. This was discarded after it had been shown that the radiation from the lamp was so very largely monochromatic ($\lambda=2537A$) and that polymerization and reaction due to straight photochemical action was negligible.

EXPERIMENTAL RESULTS

In a preliminary series of some fifty experiments a number of facts were ascertained with respect to the reactions occurring in the experimental arrangement already described. The quantitative data are not given because they lack intercomparability due to incomplete attainment of uniform operating conditions. The variations of intensity due to the transformer and mercury deposition inside the arc system have already been noted. It was also found that the velocity of reaction was also very sensitive to the mercury vapor content of the air between the arc and quartz reaction vessel. During the night in a closed laboratory the mercury vapor concentration of the laboratory air increases to such a degree that initial reaction velocities are slow due to absorption of resonance radiation outside the reaction vessel. On operating the arc this mercury is slowly removed by photosensitized oxidation and the reaction velocity in the hydrogen-ethylene system correspondingly increases. Ventilation of the room by clean air from the outside produced a similar acceleration due to removal or decrease of mercury vapor.

From this series of experiments the following conclusions could certainly be drawn. The reaction proceeded steadily until all the ethylene was consumed at which point the pressure change ceased abruptly. At this point it was always found that the pressure of condensible gas in the residue was about one-half of the ethylene pressure admitted. This points to the production not of ethane but of butane. That the product was not ethane was shown by combustion over copper oxide. The carbon dioxide formed corresponded to a hydrocarbon between C_3H_8 and C_4H_{10}. Further, the bulk of the gaseous product condensed in liquid air was also condensible in melting ethyl acetate (m.p. $= -82.4°C$) at which temperature ethane has a vapor pressure of >760 mm. This observation is true for deutero-ethylene reactions as well as for ethylene, the pressure of gases condensible in liquid air being slightly higher in the deutero-ethylene case. Here also, however, combustion pointed to a product with a formula between C_3 and C_4. This result was obtained irrespective of variations in concentration ratio, pressures or velocity of reaction (intensity). In this respect it is in disagreement with the earlier results of Taylor and Hill.[3] In their experiments with concentrations of hydrogen up to 50 percent, saturated hydrocarbons with composition between C_3 and C_4 were frequently obtained, but with higher hydrogen concentrations the saturated product approached more and more to C_2. One possible explanation of the discrepancy is suggested by the observation that, in the present series of experiments, it was never possible to show the formation of any important amount of methane. The highest recorded methane pressure in the preliminary series was 0.05 cm with hydrogenations of ethylene within the pressure range 1–11 cm. Taylor and Hill[3] continuously found marked amounts of methane, especially when reaction was prolonged beyond the end-point as recorded by pressure change. It would appear that this methane arose in part, if not wholly, from interaction of atomic hydrogen with polymeric products $(CH_2)_n$ always laid down by prolonged illumination in presence of excited mercury. Indeed methane and $(CH_2)_n$, a liquid polymer, are the final products of prolonged illumination of any hydrogen-hydrocarbon mixture, saturated or unsaturated, with excited mercury. In hydrogen rich mixtures, especially with a reaction vessel covered internally with (CH_2) polymer, methane formation is increasingly possible. In the present experiments any such deposit was removed after each experiment by oxidation with air at the high temperature of the blowpipe flame. We, therefore, conclude that in clean vessels the predominant saturated product is butane C_4H_{10}.

Quantitative data

The quantitative results were obtained in a continuous series of experiments over a period of forty hours where all conditions controlling uniformity of operation were carefully observed. All these experiments were carried out in the reaction vessel covered with mercury droplets on the side opposite to that through which the light entered, in order to secure continuous saturation

TABLE I. *Influence of ethylene and of hydrogen concentrations on their photosensitized interaction.*

No. of Expt.	P_{H_2} cm	$P_{C_2H_4}$ cm	ΔP cm	C.G. cm	t' in min.	Time in min.	Nature of Ethylene
Influence of Ethylene Concentration							
29	30.10	10.03	9.97	5.36	28	53	D
30	30.02	10.00	9.98	4.86	34	66	H
31	30.34	4.99	4.97	2.71	13.5	26	D
32	30.41	4.98	5.02	2.39	15.5	31	H
33	30.08	2.89	2.98	1.36	10.0	20	H
34	30.15	2.96	3.02	1.49	7.5	16	D
37	5.14	3.00	3.05	1.36	14.2	28	H
38	5.28	2.98	2.94	1.76	11.7	23	D
39	5.08	0.98	0.93	0.56	5.5	11	D
40	5.18	0.98	1.01	0.54	8.5	16	H
Influence of Hydrogen Concentration							
33	30.08	2.89	2.98	1.36	10	20	H
34	30.15	2.96	3.02	1.49	7.5	16	D
35	15.28	2.96	2.94	1.68	8.7	17	D
36	15.42	2.96	2.93	1.49	10.7	21	H
37	5.14	3.00	3.05	1.36	14.2	28	H
38	5.28	2.98	2.94	1.76	11.7	23	D
41	2.00	2.96	2.97	0.97	23.5	40	H
42	2.12	2.96	2.86	1.50	20.7	35	D
43	0.77	3.00	2.71	—	45.7	65	D
44	0.75	2.99	2.85	—	38.5	60	H
45	0.00	2.94	2.68	—	51.5	70	H
46	0.00	2.96	2.35	—	75.0	90	D
Influence of Deuterium Content							
106	14.98	2.98				19	HD
107	15.09	2.97			9.8	21	HD
111	—	2.98			62.5		HD
112	—	2.97					HD

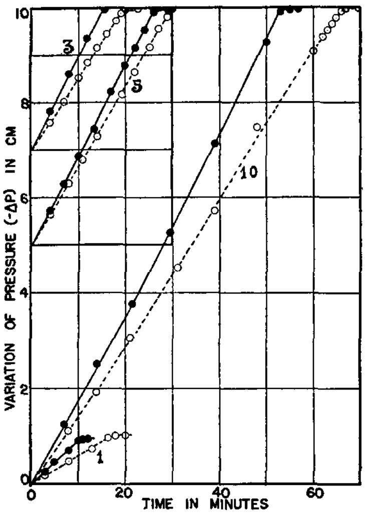

FIG. 2. Velocity of hydrogenation at varying ethylene pressures. $P_{H_2}=30$ cm. $P_{C_2H_4}=1$, 3, 5 and 10 cm. Open circles, C_2H_4; filled circles, C_2D_4.

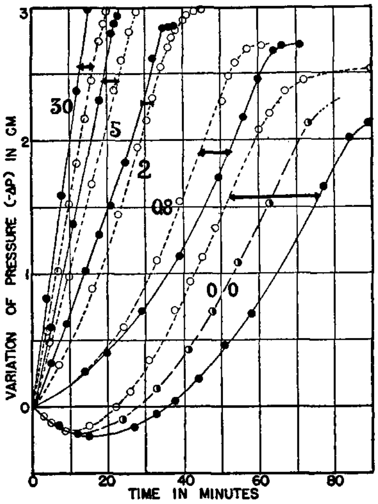

FIG. 3. Influence of hydrogen pressure at constant ethylene pressure (3 cm). $P_{H_2}=30$, 5, 2, 0.8 and 0.0 cm. Filled circle, C_2D_4; half-filled circle, $C_2H_2D_2$; open circle, C_2H_4.

of the reaction mixture with mercury vapor. The forty-hour period of experiments succeeded a period of one day in which the arc was operated to secure a steady state. The data secured in these runs are tabulated in Table I and shown graphically in Figs. 2 and 3. The first ten experiments show the influence of variation in ethylene concentration at two hydrogen pressures 30 and 5 cm. The final twelve experiments concern the influence of variation in hydrogen pressure at an ethylene pressure of ~3 cm. The final column shows whether the ethylene studied was C_2D_4(D) or C_2H_4(H). The preceding column shows the times *t* at which reaction, as measured by pressure change, was complete. In the last four experiments this time is uncertain, as can be seen from Fig. 2, the process occurring being predominantly polymerization. The sixth column gives the time *t′* required to produce a decrease in pressure equal to one-half the initial pressure of ethylene. For the reactions with high ethylene content this is not equal to the time of half-reaction since in these cases the change in pressure was not equal to $P_{C_2H_4}$. The column headed C.G. confirms the result obtained in the preliminary experiments that the condensible residue is approximately one-half the pressure of the ethylene consumed, somewhat greater with deutero-ethylene than with ethylene. The concordance of the columns $P_{C_2H_4}$ and ΔP shows that the pressure change is equal to the ethylene pressure within the experimental error, for mixtures rich in hydrogen.

The velocity data for the same experiments are presented graphically in Figs. 2 and 3. It is at once obvious that the hydrogenation of ethylene-d_4 is faster than the hydrogenation of ethylene. Only at very low hydrogen pressures when the predominant process is one of polymerization is the relation reversed, the polymerization of ethylene-d_4 being slower than that of ethylene.

With mixtures of 15 cm hydrogen and 3 cm $C_2H_2D_2$ the reaction was complete in 19 minutes exactly intermediate to the times recorded in experiments 35 and 36 for the corresponding reaction mixtures with C_2D_4 and C_2H_4. As shown in Fig. 3, the rate of polymerization of $C_2H_2D_2$ is also approximately the mean of those of C_2H_4 and C_2D_4. Since the method of preparation of $C_2H_2D_2$ was entirely different from that of the other two ethylenes, these results indicate that the divergences in rate between the proto- and deutero-ethylenes are not due to fortuitous impurities but are determined by the extent of deutero-substitution.

DISCUSSION OF RESULTS

The results of this research clarify considerably the problem of mercury sensitized hydrogenation of ethylene when compared with the data of previous work. It is now evident that, in clean quartz reaction vessels, with sufficient hydrogen present, the predominant product is butane. In no other way can the ratio of condensible gas in the product to ethylene reacted be explained. Several alternatives are exhibited by the following equations:

$$C_2H_4+H_2=C_2H_6 \qquad \text{C.G.} : \Delta P=1:1$$
$$2C_2H_4+H_2=C_4H_{10} \qquad \text{C.G.} : \Delta P=1:2$$
$$C_2H_4=(CH_2)_n(\text{liq}) \qquad \text{C.G.} : \Delta P=0:1.$$

In each case $\Delta P=P_{C_2H_4}$ for complete reaction, and C.G. refers to gaseous product condensible in liquid air.

In the first eighteen experiments of Table I, the condensible gas, with ethylene, is in every case close to and actually slightly less than one-half of the ethylene disappearing. It would be surprising if this were due to a fortuitous combination of ethane and butane formation with the right amount of polymerization (to liquid $(CH_2)_n$) to give the observed ratio of $\frac{1}{2}$, especially with the wide ethylene : hydrogen ratios studied. With ethylene-d_4 the ratio of condensible gas to ethylene reacted is in every case somewhat larger than $\frac{1}{2}$ so that we must conclude that, in this case, there is a greater tendency to form ethane-d_4 than to form ethane from ethylene.

With $P_{H_2}=30$ cm and a ratio equal to or greater than $3H_2:1C_2H_4$ or C_2D_4 the velocity of hydrogenation with either isotopic ethylene is practically independent of the ethylene concentration, as can be seen from curves 3, 5 and 10 of Fig. 2. This points to a practically quantitative acceptance of the resonance energy of the mercury by hydrogen and consequent formation of atomic hydrogen. In these experiments therefore we may write the initial process as

$$H_2+Hg'\rightarrow HgH+H\rightarrow Hg+2H. \qquad (1)$$

To yield butane we suggest that this reaction is followed by

$$H+C_2H_4=C_2H_5, \qquad (2)$$

$$C_2H_5+C_2H_5=C_4H_{10}. \qquad (3)$$

The small yield of C_2H_6 is evidence that the reaction

$$C_2H_5+H_2=C_2H_6+H \qquad (4)$$

is of low probability and this agrees with previous estimates of the activation energy for reaction (4), $E>11$ kcal.[5, 6] The more probable reaction for the production of ethane is the disproportionation reaction,

$$C_2H_5+C_2H_5=C_2H_4+C_2H_6. \qquad (5)$$

Our ratios of condensible product to ethylene reacted would indicate that this reaction (5) is a little more probable when the radical is C_2D_4H than when it is C_2H_5. Since the product, in either case, is predominantly butane, reaction (3) would appear to have a smaller activation energy than reaction (5). This conclusion appears to be in conflict with some older work by Job and Emschwiller[7] on the photolysis of liquid ethyl iodide. They found predominantly ethane and ethylene with but little butane. This is probably due to the liquid phase conditions and more especially to complex reactions involving iodine atoms. We hope to control this result by studies in the vapor phase using a new technique recently developed by one of us for the photodecomposition of ethyl iodide to yield ethyl groups.[8] The data of Norrish and Appleyard[9] on the photolysis of methyl ethyl ketone vapor indicate that quite considerable association of the radicals to form ethane, propane and butane occurred. This points to reaction (3) rather than reaction (5).

The low production of ethane indicates also that the process

$$C_2H_5+H=C_2H_6 \qquad (6)$$

is not important in comparison with (3). We attribute this to a low stationary state concentration of atomic hydrogen compared with C_2H_5 which latter governs the rate of (3). We find the reason for this in the occurrence of reaction (2) consuming hydrogen atoms with formation of ethyl. The inhibitory action of ethylene in chain reactions involving radicals and atomic hydrogen is well known[10] and may be explained by the occurrence of reaction (2). We cite the almost negligible formation of methane as another evidence of low hydrogen atom concentration since these atoms, at ordinary temperatures, give

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[6] Trenner, Morikawa and Taylor, J. Chem. Phys. **5**, 203 (1937).

[7] Job and Emschwiller, Comptes rendus **179**, 52 (1924).

[8] Jungers and Joris, Bull. Soc. Chim. Belg. **47**, 135 (1938).

[9] Norrish and Appleyard, J. Chem. Soc. 874 (1934).

[10] Staveley, Proc. Roy. Soc. **A162**, 557 (1937).

considerable C–C bond splitting with formation of methane.[6]

For similar reasons we assume that the following possible sequence for butane formation,

$$H+C_2H_4=C_2H_5, \quad (2)$$

$$C_2H_5+C_2H_4=C_4H_9, \quad (7)$$

$$C_4H_9+H=C_4H_{10}, \quad (8)$$

is less important than (2) and (3). That polymerization is a relatively slow process is suggested by our earlier work on ethylene polymerization, with methyl radicals from the photolysis of acetone,[11] where rapid reaction occurred only above 140°C. This is confirmed also by the experiments with ethyl iodide as the source of the radicals.[8] Also, if this sequence were the mode of production of butane we should not expect the hydrogenation of ethylene-d_4 to be faster than that of ethylene, a fact which is abundantly clear from all our data. For, reaction tion (7) is an essential step in the polymerization mechanism and our measurements with hydrogen absent or even in small concentrations clearly indicate that the polymerization of ethylene-d_4 is *slower* than that of ethylene. (Curves 00 of Fig. 3.)

The pairs of curves 30, 5 and 2 of Fig. 3 indicate that, at constant ethylene pressure, 3 cm, the velocity is very little dependent on the hydrogen pressure between the limits of 5 and 30 cm. Coupled with the practical independence of ethylene concentration, deduced from curve pairs 3, 5 and 10 of Fig. 2, this leads to the conclusion that with mixtures rich in hydrogen the hydrogenation process is practically zero order with respect to the two reactants.

With $P_{H_2}=5$ cm or less and $P_{C_2H_4}=1$–3 cm there is evidence that not all the resonance radiation is taken by the hydrogen. The rate of hydrogenation progressively decreases with decrease of hydrogen content and the character of reaction changes toward polymerization. When hydrogen is absent there is, in agreement with earlier findings,[12] first a pressure increase and then a decrease. The interval during which an increase is observed is more prolonged with ethylene-d_4 than with ethylene, which is in accord with the slower velocity of polymerization. The pressure increase has already been identified[12] with the initial formation of hydrogen and acetylene. In our experiments with low or zero hydrogen concentrations we have noted the yellow polymer, cuprene, characteristic of acetylene polymerization. We hope later to test whether the polymerization process may not always require small concentrations of hydrogen for its occurrence under these conditions of excitation by resonance radiation.

The quantitative anslysis of the velocity data would require measurements on the quenching efficiencies of the molecules of ethylene and ethylene-d_4. Neither of these have been studied. The small variations in the velocities of hydrogen rich mixtures, represented by the appropriate curves in both Figs. 2 and 3 can be approximately related with each other on the assumption that hydrogenation is determined by the resonance radiation absorbed by the hydrogen in the mixture of gases, the ethylenes quenching in proportion to their partial pressures with an efficiency somewhat less than that of hydrogen. It is known that the relative quenching efficiency of ethane is only of the order of 5 percent of that of hydrogen, but it is known also that the unsaturated hydrocarbons are more efficient than the saturated as quenching agents.[13] From the data it is not possible to decide whether there are material differences between the quenching efficiencies of ethylene and ethylene-d_4. The velocities obtained are also dependent on the rates of the two association reactions (2) and (3). The faster rate of hydrogenation with ethylene-d_4 would point to a greater probability of these processes with the deutero-compound than with ethylene. The slower rate of polymerization of the ethylene-d_4 is most readily interpreted on the basis of a larger energy of activation in the polymerization step (7), probably involving the zero-point energies of the molecules C_2H_4 and C_2D_4, respectively. We hope later to test this with free radicals from photodecomposition of organic molecules as the starting agents in the polymerization chain.

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[11] H. S. Taylor and J. C. Jungers, Trans. Faraday Soc. **33**, 1353 (1937).

[12] Bates and Taylor, J. Am. Chem. Soc. **49**, 2438 (1927).

[13] Bates, J. Am. Chem. Soc. **52**, 3825 (1930); **54**, 569 (1932).