The rate of peroxide decomposition is constant in homogeneous solution and is independent of the iodine concentration. The apparent relative rate of iodine consumption per mole of peroxide consumed is a complex function of the initial concentrations. Evidence that benzoyl hypoiodite accumulates in solution is discussed.

AMES, IOWA RECEIVED APRIL 5, 1950

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF CALIFORNIA, LOS ANGELES]

The Photolysis of Aliphatic Aldehydes. XIII. Acetaldehyde-*d*

BY F. E. BLACET AND R. K. BRINTON[1]

Work reported earlier[2,3] indicated that the absorption of ultraviolet light by acetaldehyde molecules may initiate either one of two primary reactions leading to decomposition.

$$CH_3CHO + h\nu \longrightarrow CH_4 + CO \qquad (1a)$$
$$CH_3CHO + h\nu \longrightarrow CH_3 + CHO \qquad (1b)$$

The intramolecular process (1a) produces the main decomposition products, methane and carbon monoxide directly, while the split into methyl and formyl radicals (1b) must be followed by various secondary reactions which will explain the formation of ethane and carbon monoxide as well as the secondary products, hydrogen, diacetyl, glyoxal, and formaldehyde, reported by Blacet and Blaedel.[4] These authors discussed the radical decomposition mechanism in the temperature range 20 to 100° as a short chain process involving the methyl radical.

$$CH_3 + CH_3CHO \longrightarrow CH_4 + CH_3CO \qquad (3)$$
$$CH_3CO \longrightarrow CH_3 + CO \qquad (4)$$

The combination of various radicals present in the system satisfactorily explains diacetyl, glyoxal, and formaldehyde production. The formation of hydrogen is possibly an interaction of formyl radicals with acetaldehyde.

$$CHO + CH_3CHO \longrightarrow H_2 + CO + CH_3CO \quad (2)$$

The work presented in this paper represents an attempt to clarify further the secondary radical reactions by a study of the photolysis of acetaldehyde-*d*, CH_3CDO. By analogy the primary steps are

$$CH_3CDO + h\nu \longrightarrow CH_3D + CO \qquad (1aD)$$
$$CH_3CDO + h\nu \longrightarrow CH_3 + CDO \qquad (1bD)$$

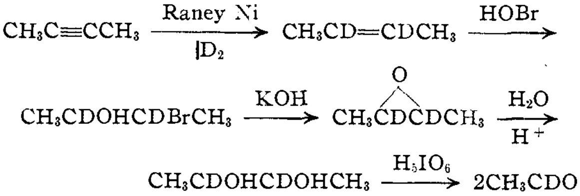
The propagation of the chain mechanism should proceed by either the capture of the acyl deuterium atom

$$CH_3 + CH_3CDO \longrightarrow CH_3D + CH_3CO \quad (3aD)$$

followed by (4) or the capture of the methyl hydrogen atom followed by a rearrangement and dissociation also into carbon monoxide and a methyl radical. A chain involving acyl hydrogen capture should lead to pure methane-*d*, CH_3D, while one brought about by methyl hydrogen capture would yield mixtures of methane and methane-*d* at low temperatures (20–100°) where the chain lengths are short, and pure methane-*d* at high temperatures where the primary yield of (1aD) is small compared to the total methane produced. The result of both chain mechanisms operating simultaneously would of course result in mixtures of methane-*d* and methane over the whole temperature range. It was thought that analysis of the photolysis products for the relative amounts of methane and the various heavy methanes and also for the other deuterated products would possibly yield valuable evidence as to the course of the secondary radical reactions.

Experimental Procedures and Results

Acetaldehyde-*d* used in the photolysis experiments was synthesized by the following reaction sequence



$$CH_3C{\equiv}CCH_3 \xrightarrow[D_2]{\text{Raney Ni}} CH_3CD{=}CDCH_3 \xrightarrow{HOBr}$$
$$CH_3CDOHCDBrCH_3 \xrightarrow{KOH} CH_3\overset{O}{\widehat{CDCD}}CH_3 \xrightarrow[H^+]{H_2O}$$
$$CH_3CDOHCDOHCH_3 \xrightarrow{H_5IO_6} 2CH_3CDO$$

The initial catalytic half reduction was carried out in a closed system by circulating deuterium gas (99.8 mole % D_2) at about 2 atm. pressure through a solution of the butyne in ether solvent. In a representative reduction 5090 ml. of deuterium was added to 10.9 g. of 2-butyne and 0.5 g. of Raney nickel catalyst[5] in 25 ml. of ether during a four-hour period. Solvent and hydrocarbon materials carried out of the solution by the 200 ml./min. deuterium gas stream were returned by a cold finger condenser at −80°. The combined yields of several reductions were converted to acetaldehyde by methods previously described.[6,7,8] The aldehyde yield from 2-butyne was 27% of the theoretical value. Purification of the acetaldehyde was effected by conversion to the alde-

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[1] Division of Chemistry, University of California, Davis, California.

[2] F. E. Blacet and J. D. Heldman, THIS JOURNAL, **64**, 889 (1942).

[3] F. E. Blacet and D. E. Loeffler, *ibid.*, **64**, 893 (1942).

[4] F. E. Blacet and W. J. Blaedel, *ibid.*, **64**, 3374 (1940).

[5] L. W. Covert and H. Adkins, *ibid.*, **54**, 4116 (1932).

[6] S. Winstein and R. E. Buckles, *ibid.*, **64**, 2784 (1942).

[7] C. E. Wilson and H. J. Lucas, *ibid.*, **58**, 2399 (1936).

[8] E. L. Jackson, "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, 1944, p. 341.

TABLE I

NON-CONDENSABLE PRODUCTS FROM ACETALDEHYDE-*d* PHOTOLYSES

All products are shown relative to CO as 1.00

Wave length, Å.	3130	3130	3130	2804	2654	2654	2537	2380	2380	2380
Aldehyde pressure, mm.	331	336	331	333	336	302	329	338	331	347
Temperature, °C	30	150	250	30	30	250	150	30	150	250
Trap temperature, °C.	−120	−190	−120	−190	−190	−120	−120	−190	−190	−120
CD_4	0.002	0 002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002
CHD_3	.003	.008	.008	.004	.006	.006	.010	.008	.012	.008
CH_2D_2	.005	.016	.018	.009	.010	.018	.016	.016	.012	.018
CH_3D	.19	.50	.54	.36	.48	.53	.48	.55	.47	.53
CH_4	.30	.43	.45	.39	.35	.45	.45	.38	.47	.46
Total methane	.50	.96	1.02	.77	.85	1.01	.96	.96	.97	1.02
D_2	.003	.004	.006	.011	.009	...	...	.040	...	...
HD	.005	.006	.010	.014	.017	...	...	.070	...	...
H_2	.005	.004	.006	.011	.009	...	...	.030	...	...
Total hydrogen	.013	.014	.022	.036	.035	...	...	.14	...	...
Total ethane	.08	...	.05	...	...	.03	.02	...	...	.03

hyde ammonia salt and regeneration with sulfuric acid.

The analysis of the heavy acetaldehyde mixture by means of a mass spectrometer has been described elsewhere.[9] Relative amounts (%) of the various acetaldehyde species present in the mixture were

CH_3CHO	17.1	CHD_2CHO	0.4
CH_3CDO	78.2	CHD_2CDO	0.7
CH_2DCHO	1.8	CD_3CHO	Trace
CH_2DCDO	1.4	CD_3CDO	0.4

The reason for the high percentage (17.1%) of undeuterated acetaldehyde in the mixture is not clear. The data of Mozingo and coworkers[10] indicate that the amount of protium initially adsorbed on the Raney nickel catalyst should be no greater than 1% of the total deuterium used in the reduction. Mass spectrometric analysis of the deuterium substrate before and after reduction showed the deuterium to be unchanged in composition. Acetaldehyde prepared either from 2-butyne which was reduced in ether solvent and/or from 2-butene in the solvent-free state had essentially the composition shown above. It is probable that the exchange of protium with deuterium in the final acetaldehyde mixture was not a result of the exchange with the 2-butyne or ether solvent in the initial catalytic reduction but rather protium–deuterium exchange with aqueous solvents in the subsequent steps.

TABLE II

NON-CONDENSABLE PRODUCTS FROM ACETALDEHYDE (CH_3-CHO) PHOTOLYSIS

All products are shown relative to CO as 1.00

Wave length, Å.	3130	3130	3130	2380	2380
Aldehyde pressure, mm.	352	348	333	344	344
Temperature, °C.	30	30	30	30	30
Trap temp., °C.	−190	−120	−120	−190	−120
CH_4	0.85	0.88	0.88	1.00	1.02
H_2	.021	.017	...	0.153	0.151
C_2H_6	...	.023	.038	...	.013

The apparatus and experimental procedures employed in the photolysis of acetaldehyde-*d* were very similar to those described in detail by Blacet and Heldman.[2] Analyses of the non-condensable gas samples were made with the Westinghouse Type LV mass spectrometer[11] instead of by the microgas technique used by these workers.

Primary standards were used for comparison in the mass spectrometric analyses wherever possible. Methane, ethane, hydrogen and carbon monoxide standards were found to be free of impurities by mass spectrometric analysis. Deuterium gas purchased from the Stuart Oxygen Co., San Francisco, analyzed 99.8% D_2. Methane-*d* was prepared by adding 99.9% deuterium oxide to methylmagnesium bromide. The composition of the final product was 97.5% CH_3D and 2.5% CH_4. Samples of hydrogen-*d* (H-D) and other heavy methanes (CH_2D_2, CHD_3, and CD_4) were not prepared. Since these products were in small quantities in all analyses, reasonable assumptions as to their mass spectra led to only small errors in their determination.

The data obtained for the analysis of the non-condensable products of a number of photolyses are shown in Tables I and II. Irradiation times of 40 to 70 hours at 30°, 6 hours at 150°, and 0.5 hour at 250° produced approximately 3% decomposition. Absorption intensities varied as much as four fold among the various runs as a consequence of different experimental conditions.

The ethane analysis is reported for only those experiments in which the separation of the two fractions was made at −120°. Condensable fractions separated at −190° contained a portion

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[9] R. K. Brinton and F. E. Blacet, *J. Chem. Phys.*, **17**, 797 (1949).

[10] R. Mozingo, D. E. Wolf, S. A. Harris and K. Folkers, THIS JOURNAL, **65**, 1013 (1943).

[11] J. A. Hipple, D. J. Grove and W. M. Hickam, *Rev. Sci. Inst.*, **16**, 69 (1945); J. A. Hipple, *Electronics*, **16**, No. 11, 120 (1943).

of the ethane product. The "total ethane" reported for photolyses of the deuterated aldehyde was composed approximately of 25% to 40% of ethane-*d*, 55% to 70% ethane, and small amounts of ethane-d_2. No standards for the heavy ethanes were used in the analyses, and also since impurities, perhaps from acetaldehyde polymerization, interfered in the ethane spectrum region, the "total ethane" estimations are of low accuracy.

The presence of ethane in the gaseous photolysis products is contrary to the findings of Blacet and Volman.[12] However, their investigation was confined to irradiation at 2654 Å. where the amount of ethane is of the order of 1% abundance and it is probable that presence of this amount of ethane could not be detected by their analytical method.

Determinations of quantum yields of carbon monoxide production at 30° for both acetaldehyde and acetaldehyde-*d* were made in a manner similar to the method described in other papers of this series. The analysis for carbon monoxide in this set of photolyses was made by the Blacet–Leighton micro analytical method. Quantum yields of carbon monoxide production, ΦCO, determined in these experiments as well as some corresponding quantum yields previously reported, are compiled in Table III.

TABLE III

QUANTUM YIELDS OF CARBON MONOXIDE FROM ACETALDEHYDE AND ACETALDEHYDE-*d* PHOTOLYSES AT 30°

Aldehyde	Wave length, Å.	Pressure, mm.	Incident intensity, ergs/sec.	ΦCO
CH_3CHO	3130	207	9,990	0.32
	3130	196	10,680	.30
CH_3CDO	3130	195	7,010	.26
	3130	194	6,620	.27
	2654	190	795	.74
	2654	187	4,330	.75
	2380	204	2,210	.96
	2380	201	1,855	1.01
CH_3CHO	3130	201	10,195	0.24[13]
	2654	198	8,800	.79[13]

Photolyses of the deuterated acetaldehyde made in the presence of about 1 mm. pressure of iodine vapor were reported previously.[9] By the use of radiation in the region 2537–2654 Å. where both radical and intramolecular processes occurred, it was possible to analyze for methane produced by the intramolecular primary process (1aD) as well as for methyl iodide formed by iodine capture of methyl radicals from process (1bD). The results from typical iodine photolyses are shown in Table IV. Also included in this table is the composition of methane that would be produced theoretically on the basis of the original aldehyde composition if all methane were a direct result of the intramolecular process (1aD).

TABLE IV

COMPOSITION OF METHANE RESULTING FROM THE PHOTOLYSIS OF ACETALDEHYDE-*d* IN THE PRESENCE OF IODINE VAPOR AT 30° WITH THE COMBINED WAVE LENGTHS 2654 AND 2537 Å.

Mole fraction	Photolysis	Calculated 100% intramolecular
CD_4	0.03	0.004
CHD_3		.007
CH_2D_2		.018
CH_3D	.764	.800
CH_4	.206	.171

The close correspondence of columns two and three of Table IV indicates that the "quenching" of the radical processes was almost complete. It is probable that the small amount of radical mechanism which evidently occurred in the iodine photolyses would have been further decreased had it been possible to obtain higher iodine vapor concentration at the temperature employed. Complete elimination of the radical mechanism would presumably lead to an exact correspondence between columns two and three of Table IV.

Discussion

(1) **Chain Mechanisms.**—A consideration of chain mechanisms may be made by an examination of the composition of the photolysis products at 150 and 250° where the principal products are quite clearly carbon monoxide and methane. A mechanism entailing an acyl hydrogen capture by methyl radicals should give about 95% abundance of the CH_3 species in the steady state methyl radical composition. Assumption of equal velocities of (3) and (3aD) would lead to a CH_3D/CH_4 ratio of 4.6 on basis of the original aldehyde composition. Although this value varies widely from the experimentally determined ratio shown in Fig. 1, a small difference (1–2 kcal.) in activation energies of (3) and (3aD) would be sufficient to account for the variance. It is significant, however, that substantial amounts of ethane-*d* and ethane-d_2 in the photolysis products would be unlikely from a system which contains such a predominance of the CH_3 species. The composition of the ethane fraction would therefore indicate that the acyl hydrogen capture mechanism is not a completely satisfactory explanation of the experimental data.

The methyl hydrogen capture mechanism for the mixture of acetaldehydes may be represented by the scheme

$$CH_3 + CH_3CHO \longrightarrow CH_4 + CH_2CHO \quad (3b)$$
$$CH_3 + CH_3CDO \longrightarrow CH_4 + CH_2CDO \quad (3bD)$$
$$CH_2D + CH_3CHO \longrightarrow CH_3D + CH_2CHO \quad (5a)$$
$$CH_2D + CH_3CDO \longrightarrow CH_3D + CH_2CDO \quad (5b)$$

Taylor and Burton[14] who originally postulated such a mechanism for the thermal decomposition of acetaldehyde suggested that the second step of

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[12] F. E. Blacet and D. Volman, THIS JOURNAL, **60**, 1243 (1938).

[13] P. A. Leighton and F. E. Blacet, *ibid.*, **55**, 1766 (1933).

[14] H. A. Taylor and M. Burton, *J. Chem. Phys.*, **I**, 675 (1939).

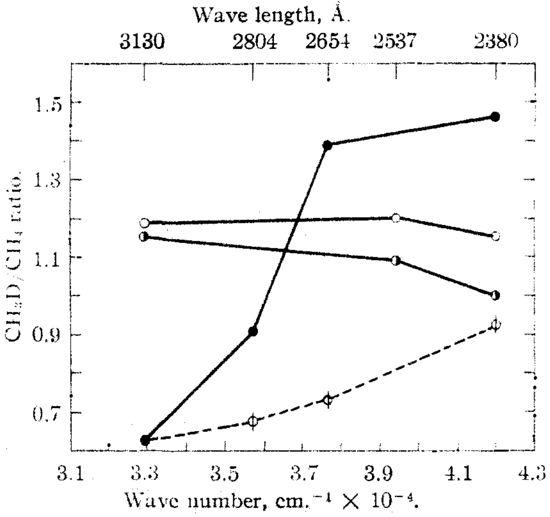


Fig. 1.—The variation of CH_3D/CH_4 with temperature and wave length ○, 250°; ◑, 150°; ●, 30°; ⦶, 30° (corrected for contribution from the intramolecular primary process).

the chain be a simultaneous rearrangement and fission to form carbon monoxide and methyl radicals

$$CH_2CHO \longrightarrow CH_3 + CO \qquad (4b)$$
$$CH_2CDO \longrightarrow CH_2D + CO \qquad (4bD)$$

In order to account for the experimental CH_3D/CH_4 ratio it would be reasonable to assume that reactions (3b) and (5a) entailing methyl radical interaction with acetaldehyde must have higher velocities than the analogous reactions of methyl radicals with acetaldehyde-*d*, (3bD) and (5b), or as an alternative, (4b) must occur at a more rapid rate than the corresponding reaction (4bD). Either or both of these possibilities are reasonable on the basis of the small difference in activation energies necessary to bring about the observed product composition.

On inspection of Table I it appears that a mixed mechanism with both acyl and methyl hydrogen capture could not exist. If this were the case reaction of the CH_2D radical with acetaldehyde-*d*

$$CH_2D + CH_3CDO \longrightarrow CH_2D_2 + CH_3CO \qquad (6)$$

would lead to substantial amounts of CH_2D_2 and other methanes of higher deuterium content. In addition, the relative amount of CH_2D_2 present should increase markedly from 30 to 150° since longer chain lengths would tend to increase the possibility of methanes of higher deuterium content. The relative amount of CH_2D_2 was almost independent of temperature and present in quantities predictable from the original aldehyde composition.

The choice between the two suggested chain decompositions is not clear cut. The composition of the ethane side product would seem to give favor to the methyl hydrogen capture mechanism. However, it is necessary that further experiments be carried out before a definite conclusion can be reached. If samples of acetaldehyde-*d* of high purity could be prepared, perhaps by other synthesis procedures, photolyses could be made in which the possibility of reactions (3), (3b), (5a), and (4b) would be eliminated. Then the choice of one of the mechanisms should not be difficult.

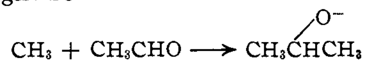
(2) **Hydrogen Formation.**—In a system where both CHO and CDO radicals are present and such a wide variety of reaction possibilities exist it is difficult to draw definite conclusions concerning mechanisms. Comparison of the results of Tables I and II does indicate that the "total hydrogen" from the photolysis of the deuterated aldehyde is about parallel to the amount of hydrogen formed from CH_3CHO photolysis under similar conditions. The composition of "total hydrogen" was approximately 50% HD, 25% H_2, and 25% D_2 in all runs made; showing no definite change with experimental conditions. It is interesting to note that the "total hydrogen" is composed of about equal quantities of protium and deuterium, a distribution varying widely from the over-all abundance of 80% H and 20% D in the original aldehyde mixture. This evidence indicates that hydrogen is produced to a large extent both at low and high temperature from the acyl part of the acetaldehyde molecule. The substantial amount of D_2 found may well be the result of CDO radical reaction with the acyl end of the acetaldehyde molecule (reaction 2). Evidence against a primary split[15] into hydrogen atom and acetyl radical is not altogether conclusive and hydrogen formation could possibly be a result of this initial reaction at short wave lengths where the energy of the quantum exceeds the C-H bond strength.

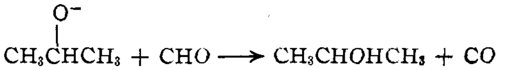
(3) **Condensation Reactions.**—At 30° and for quanta of lower energy values it is apparent that the chain mechanisms previously discussed are not adequate to explain all the experimental data. Since hydrogen is produced in small amounts, most formyl radicals produced in the primary process must react without hydrogen formation. In addition some type of methyl radical "condensation" must take place to explain a total methane/carbon monoxide ratio appreciably less than unity. Since the combination of methyl radicals to form ethane is insufficient to account for the low value of the ratio, and since the removal of formyl radicals by combination to form glyoxal and formaldehyde[4] tends to increase rather than decrease this ratio, removal of methyl radicals without carbon monoxide disappearance must be an important side reaction. A mechanism similar to one employed by Rust, Seubold and Vaughan[16] to

[15] E. W. R. Steacie, "Atomic and Free Radical Reactions," New York, N. Y., 1946, pp. 181-198.

[16] F. F. Rust, F. H. Seubold and W. E. Vaughan, THIS JOURNAL, **70**, 4253 (1948).

explain formation of di-*n*-propylcarbinol in the peroxide catalyzed decomposition of *n*-butyraldehyde could offer a possible explanation of these discrepancies. For acetaldehyde a typical mechanism might be


$$CH_3 + CH_3CHO \longrightarrow CH_3\overset{O^-}{C}HCH_3 \quad (7)$$


$$CH_3\overset{O^-}{C}HCH_3 + CHO \longrightarrow CH_3CHOHCH_3 + CO \quad (8)$$

Evidence for the existence of such a decomposition sequence would rest on the identification of isopropyl alcohol in the condensable products. Qualitative mass spectrometric investigation gave some evidence of the presence of isopropyl alcohol and acetone, possibly as a consequence of methyl and acetyl combination, but positive identification was difficult because of screening of the spectra of these compounds by aldehyde polymer fractions. The approach of the methane/carbon monoxide ratio to unity at shorter wave lengths and higher temperatures may well be attributed to instability of the condensed methyl–acetaldehyde radical formed in reaction (7) and its dissociation into methane and an acetyl radical.

Acknowledgment.—The mass spectrometer used for analytical purposes in these studies was a gift to the University of California, Los Angeles, by the Signal Oil and Gas Co., of Los Angeles. During the period of study the second-named author was holder of the H. M. Mosher Fellowship established by this same company. The research project of which this study was a part, has received financial aid from the Research Corporation, New York.

Summary

The photochemical behavior of a mixture of acetaldehyde and acetaldehyde-*d* has been investigated from 30 to 250° in the wave length region 3130 to 2380 Å. The variation in the ratio of methane-*d* to methane (CH_3D/CH_4) was studied in detail. The amount of CH_4 formed under all conditions was relatively much higher than would be predicted from the composition of the aldehyde mixture if analogous reactions involving similar species containing hydrogen or deuterium atoms had equal velocities. The ratio of CH_3D/CH_4 at 30° varied from 0.63 at 3130 Å. to 1.46 at 2380 Å. and at 250° from 1.19 at 3130 Å. to 1.15 at 2380 Å.

The probability of various type chain mechanisms involving the methyl radical have been discussed. On the basis of experimental evidence no definite choice could be made between a mechanism involving the capture of the acyl hydrogen atoms of acetaldehyde molecules by methyl radicals and one by which the methyl hydrogen atoms were removed from the parent molecules. The presence of appreciable ethane-*d* and ethane-d_2 in the products may be regarded as some evidence in favor of the methyl hydrogen capture mechanism. Evidence is presented which indicates that both mechanisms were not operating simultaneously.

The distribution of H and D in the hydrogen formed during photolysis is greatly different from the distribution in the original aldehyde mixture. Hydrogen is evidently formed mainly from the acyl part of the acetaldehyde molecule.

The excess of carbon monoxide over methane in photolyses at 30° and long wave lengths necessitates the existence of some type of condensation reaction for methyl radicals. The removal of methyl radicals by combination with acetaldehyde molecules to give a condensed radical and subsequent combination of this radical with formyl radicals to yield carbon monoxide and isopropyl alcohol may be a possible explanation.

LOS ANGELES, CALIF. RECEIVED JANUARY 24, 1950

[FROM THE KODAK RESEARCH LABORATORIES, COMMUNICATION NO. 1318]

The Use of the Stationary Platinum Microelectrode in the Determination of Half-Wave Potentials

BY D. B. JULIAN AND W. R. RUBY

In the polarographic study of the oxidation–reduction potentials of some substituted *p*-phenylenediamines used as photographic developers, certain limitations of the dropping mercury electrode precluded its use. For this reason, an investigation was made of the behavior of the platinum microelectrode as the polarizing electrode in the determination of half-wave potentials. The application of solid metal microelectrodes to polarographic determinations has been investigated by a number of workers.[1–6]

A careful and extensive investigation by Laitinen and Kolthoff[1] of the stationary platinum electrode has shown that a steady state is obtained, if one waits for several minutes after applying each increase in voltage. Based upon this work and

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[1] H. A. Laitinen and I. M. Kolthoff, THIS JOURNAL, **61**, 3344 (1939).

(2) O. H. Müller, *ibid.*, **69**, 2992 (1947).

(3) S. I. Sinyakova, *Trudy Vsesoyuz Konferentii Anal. Khim.* (Proceedings of the All-Union Conference of Analytical Chemistry), **2**, 529 (1943).

(4) E. M. Skobets, L. S. Berenblum and N. N. Atamanenko, *Zavodskaya Laboratoriya* (*U.S.S.R.*), **14**, 131, No. 2 (1948).

(5) S. D. Miller, *Trudy Vsesoyuz Konferentii Anal. Khim.*, **2**, 551 (1943).

(6) Yu. S. Lyalikov and V. I. Karmazin, *Zavodskaya Laboratoriya* (*U.S.S.R.*), **14**, 138, No. 2 (1948).