Liquid Acetylene. Metalation and Carbonation Studies

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The novel use of liquid acetylene as both reactant and solvent under pressure below its critical temperature is reported. Alkali metals such as lithium, sodium and potassium are rapidly converted into the corresponding acetylides in high conversion using excess liquid acetylene containing catalytic amounts of ammonia or trimethylamine. Acetylide formation also takes place in undiluted liquid acetylene, but at a slower rate. A mechanism for acetylide formation in this medium and in the presence of catalytic amounts of donor molecules is discussed. A simple, one-step method for the preparation of sodium propiolate by the reaction of sodium, liquid acetylene and liquid carbon dioxide is presented. Trimethylamine is a highly effective catalyst for this system, although metalation and carbonation to sodium propiolate is possible in its absence.

Although the use of gaseous[1] and solvated acetylene[2,3] in synthetic operations is well documented, the use of the liquified gas as both reactant and solvent has been scarcely studied. Industrial explosions[4,5] at the turn of the century and the fact that the pure or diluted liquid can be detonated *via* ignition of the vapor phase[6] may explain this lack of interest.

The polymerization[7] of liquid acetylene has been claimed to yield *cis*-polyacetylene *via* a cationic mechanism. Also, the interaction of liquid acetylene with dimethyl and diethyl ethers yielded 1:1 complexes at temperatures below −100°, while attempts to chlorinate the liquid often resulted in explosions.[8,9]

Our object in studying liquid acetylene as a solvent–reactant system was to determine if it could be handled safely in synthetic operations, and to assess any possible mass action or solvation effects (faster rate, higher conversion, better product purity) which might benefit acetylene reactions, such as metalation, ethynylation, carbonation or complex formation. To guard against accidental explosion or detonation, work was generally carried out below the critical temperature of acetylene in a suitably designed pressure system, in an isolated building.

Recently, a barricaded reaction system for observing and carrying out reactions in liquid acetylene safely under pressure up to its critical temperature (35°) has been described.[10] Liquid acetylene was exposed to both polar and nonpolar diluents, and also to the action of alkali metal hydroxides to yield a variety of complexes. This reaction system was operated repeatedly during a 10-month period with no explosions or exothermic decompositions noted, and is the basis for new work reported in this publication.

Alkali Metal Acetylide Formation.—Table I shows that alkali metals (either as dispersions or coarse particles) react readily with liquid acetylene in the presence of catalytic to small amounts of ammonia. Sodium could also react with liquid acetylene, in the absence of ammonia, to give a 75% conversion to sodium acetylide in 5.5 hr. However, the reaction rate was considerably enhanced by the presence of ammonia. Essentially quantitative yields of acetylide could be realized in 1–3 hr using reaction loadings of 0.10–0.34 mol of alkali metal, 0.05–0.41 mol of NH_3 and 0.60–1.00 mol of liquid acetylene. Ammonia, used catalytically (0.5 mol of ammonia/g-atom of sodium) still effected a rapid, quantitative conversion to acetylide using a reaction loading of 0.1 g-atom of sodium, 0.60 mol of acetylene and 0.05 mol of ammonia. Similar results were also obtained with trimethylamine, the acetylide being used to synthesize sodium propiolate from Na, liquid C_2H_2 and CO_2 (*cf.* carbonation of sodium acetylide to sodium propiolate).

The use of excess liquid ammonia as a reaction solvent for acetylide formation and ethynylation is well known,[11] but its use as a catalyst in a liquid acetylene system has never been reported. Limited work with potassium and lithium showed that the respective acetylides were also readily formed in liquid acetylene. The lithium derivative, in contrast, disproportionated readily to the carbide (Li_2C_2) on standing at ambient room temperature. However, it is reported to be stabilized effectively by complexing with ethylenediamine.[12] The lower purity values (Table I) obtained for the dry, isolated acetylides, based on evolved acetylene, are believed due to moisture absorption during isolation and analysis. Some slow disproportionation to the carbide derivative on standing is also possible.

When all gaseous products (Table II) derived from the reaction of 0.20 g-atom of Na, 0.90 mol of liquid C_2H_2 and 0.05 mol of NH_3 were subjected to vapor chromatographic analysis for acetylene, ethylene, ethane and hydrogen, no hydrogen was observed, but the total moles of ethylene and ethane formed showed a 99% conversion to sodium acetylide based on eq 6 and 11. This value agreed well with the 98% conversion based on the weight of isolated acetylide (Table I, expt 5). Complete analysis of the total vapor and liquid phases (Table III) gave similar results with only a trace of hydrogen now detected. The above results show conclusively that alkali metal acetylides are formed in high conversion in the liquid acetylene system using a small amount of a basic catalyst.

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[1] J. W. Copenhaver and M. H. Bigelow, "Acetylene and Carbon Monoxide Chemistry," Reinhold Publishing Corp., New York, N. Y., 1949.

[2] E. D. Bergmann, "The Chemistry of Acetylene and Related Compounds," Interscience Publishers, New York, N. Y., 1948.

[3] R. A. Raphael, "Acetylenic Compounds in Organic Synthesis," Academic Press, New York, N. Y., 1955.

[4] J. M. Crafts, *Science*, **3**, 377 (1896).

[5] S. A. Miller, "Acetylene," Vol. I, Academic Press, New York, N. Y., 1955, p 11.

[6] H. A. Mayes and H. J. Yallop, *The Chemical Engineer*, 25 (Jan–Feb 1965).

[7] Y. Tobata, *et al.*, *Kogyo Kagaku Zasshi*, **65**, 731 (1962).

[8] G. Baume and A. F. O. Germann, *C. R. Acad. Sci., Paris*, **153**, 569 (1911).

[9] Fiat Final Report No. 1017, PB 60886.

[10] R. J. Tedeschi, *et al.*, *Process Design Develop.*, **7**, 303 (1968).

[11] See ref 3, p 10, and references cited therein.

[12] O. F. Beumel, Jr., and R. F. Harris, *J. Org. Chem.*, **28**, 2775 (1963).

TABLE I

PREPARATION OF ALKALI METAL ACETYLIDES IN LIQUID ACETYLENE

Expt no.	Amt, mol				Reaction			Isolated acetylide		
	Metal		C_2H_2	NH_3	Temp, °C	Pressure, psig	Time, hr	Purity based on Metal	Purity based on C≡CH	Convn based on wt, %
1	0.10	Na	0.60	0.41	8–25	360–400	1.25	96	86	100
2	0.10	Na	0.60	0.10	5–21	400–478	2.5	96	86	102
3	0.10	Na	0.60	0.05	17–25	420–620	3	97	92	102
4	0.20[a]	Na	0.00	0.80	22–24	80–82	2			
5	0.20	Na	0.90	0.05	11–26	540–692	3	*c*		98
6	0.20[b]	Na	0.90	0.05	5–30	610–745	0.5	*d*	73	87
7	0.10	Na	0.45	0.00	21–26	520–560	5.5	*d*	62	75
8	0.10	K[f]	0.60	0.20	26–30	349–380	3	99	85	91
9	0.34	Li[e]	1.00	0.20	18–32	475–598	3			96

[a] Reaction of sodium dispersion with liquid ammonia in the absence of liquid acetylene, to determine if sodamide is formed as a reaction intermediate. No sodamide was formed. [b] Short reaction time; total reaction phases (liquid and gas) analyzed for C_2H_2, C_2H_4 and C_2H_6 by vapor fractometry (*cf.* Table III, expt A). [c] Product not analyzed for NaC_2H. However, vapor fractometry analyses for acetylene, ethylene and ethane material balance shows a 99% conversion to acetylide, which agrees well with 98% conversion based on weight (9.4 g) of isolated acetylide (*cf.* Table II). [d] Incomplete conversion based on isolated yield of acetylide; Na values have no significance hence not reported. [e] Lithium acetylide is not stable. It decomposed to the carbide (Li_2C_2) on standing a total of 7 days and lost weight gradually (10.5 → 6.1 g.) [f] Some loss (undetermined) of potassium sand on transfer and decantation; hence yield obtained is a minimum figure.

TABLE II

SODIUM ACETYLIDE FORMATION.[a] ANALYSIS OF REACTION VAPOR PHASE[b] BY GAS CHROMATOGRAPHY

Time, hr	Temp, °C	Ethane, %	Ethylene, %	Acetylene, %	Hydrogen, %
0[c]	8	0	0	100	0
0.12	28	0	1.5	98.5	0
0.15	0	0.3	2.7	97.0	0
0.50	26	0.3	3.2	96.5	0
1.00	24	0.4	3.5	95.9	0
1.50	22	0.3	3.8	96.0	0
3.00	21	0.5	4.1	95.4	0

[a] Reaction charge: 0.20 mol of Na, 0.90 mol of C_2H_2, 0.05 mol of NH_3 (*cf.* Table I, expt 5), % conversion to NaC_2H, 99%. [b] Only gas phase analyzed by careful venting to an evacuated gas sampling bottle (50 cc). [c] Sample taken 7 min after liquefication of acetylene and prior to ammonia addition. Zero reaction time defined as time of ammonia addition.

TABLE III

SODIUM ACETYLIDE FORMATION. ANALYSIS[a] OF REACTION LIQUID AND VAPOR PHASES BY GAS CHROMATOGRAPHY

	Temp, °C	Time, hr	% H_2	% C_2H_6	% C_2H_4	% C_2H_2	% N_2
A[b]	5–30	0.5	<0.1	0.3	2.4	56.3	41
B[b]	21–26	5.5	0.1	0.3	1.8	60.0	38

[a] Samples A and B were obtained by venting the reaction mixture slowly into a 32.8-l. steel gas tank followed by dilution with nitrogen to a total pressure of 800 mm. Before dilution, sample A exerted 520-mm pressure at 20°, sample B, 475 mm at 19°. [b] Reaction charges: sample A, 0.20 mol of Na, 0.90 mol of C_2H_2, 0.05 mol of NH_3 (*cf.* Table I, expt 6); sample B, 0.10 mol of Na, 0.45 mol of C_2H_2 (*cf.* Table I, expt 7).

Mechanism of Acetylide Formation.—The catalytic effect realized with both ammonia and trimethylamine in acetylide formation is best explained by the anion-radical mechanism shown below.

Support for such a mechanism is the extensive work reported in recent years on the formation and properties of solvated electrons, of which alkali metal–ammonia or amine solutions are prime examples.[13] Also, the reaction of diphenylacetylene (tolan) with alkali metal hydrocarbons in THF has been stated to involve intermediate anion-radical formation.[14]

The almost complete absence of free hydrogen and the formation of ethylene and ethane (Tables II and III) during the reaction also supports such a route. In contrast, acetylide formation in organic solvents[15] is accompanied by a preponderance of hydrogen evolution, although some reduction of acetylene is also noted.

Further, the reaction of sodium with ammonia under identical conditions yielded no sodamide showing this species is not present as a reaction intermediate during metallation in liquid acetylene. Traces of iron salts and air are necessary catalysts for the conversion of sodium to sodamide in liquid ammonia.[16,17] Sodamide, in turn, reacts rapidly with acetylene in liquid ammonia to form sodium acetylide quantitatively.[18] The over-all route to acetylide can be regarded as proceeding through two stages. The first (steps 1–6) accounts primarily for by-product ethylene, while the second (minor route) (steps 7–11) yields ethane.

$$\mathrm{Na\cdot + NH_3 \leftrightarrows Na^+[NH_3]\cdot^-} \qquad (1)$$

$$\mathrm{CH{\equiv}CH + Na^+[NH_3]\cdot \rightleftarrows \underset{I}{\cdot[CH{=}\ddot{C}H]Na^+} + NH_3} \qquad (2)$$

$$\mathrm{I + CH{\equiv}CH \longrightarrow \underset{II}{[CH_2{=}\dot{C}H]} + NaC{\equiv}CH} \qquad (3)$$

$$\mathrm{II + Na^+[NH_3]\cdot^- \longrightarrow \underset{III}{[CH_2{=}\ddot{C}]^-Na^+} + NH_3} \qquad (4)$$

$$\mathrm{III + CH{\equiv}CH \longrightarrow CH_2{=}CH_2 + NaC{\equiv}CH} \qquad (5)$$

Over-all route

$$\mathrm{3CH{\equiv}CH + 2Na \longrightarrow 2NaC_2H + CH_2{=}CH_2} \qquad (6)$$

The further reaction of ethylene with ammoniated sodium $[Na^+NH_3]\cdot^-$ will eventually yield ethane (steps 7–11).

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(13) U. Schindewolf, *Angew. Chem. Intern. Ed. Engl.*, **7** [3], 190 (1968).

(14) D. A. Dadley and A. G. Evans, *J. Chem. Soc., B*, 418 (1967); 107 (1968).

(15) T. F. Rutledge, *J. Org. Chem.*, **22**, 649 (1957).

(16) K. W. Greenlee and A. L. Henne, *Inorg. Syn.*, (2) **75**, 79 (1946).

(17) T. H. Vaughn, *et al.*, *J. Amer. Chem. Soc.*, **56**, 2120 (1934).

(18) See ref 3, p 193.

$$Na^+(NH_3)\cdot^- + CH_2{=}CH_2 \longrightarrow \underset{IV}{{}^-[\ddot{C}H_2\dot{C}H_2]Na^+} + NH_3 \quad (7)$$

$$IV + CH{\equiv}CH \longrightarrow \underset{V}{[CH_3\dot{C}H_2]} + NaC{\equiv}CH \quad (8)$$

$$V + Na^+(NH_3)\cdot^- \longrightarrow \underset{VI}{{}^-[CH_3CH_2]Na^+} + NH_3 \quad (9)$$

$$VI + CH{\equiv}CH \longrightarrow CH_3CH_3 + NaC{\equiv}CH \quad (10)$$

Over-all route

$$2Na + CH_2{=}CH_2 + 2CH{\equiv}CH \longrightarrow 2NaC_2H + CH_3CH_3 \quad (11)$$

Total stoichiometry for both stages

$$5CH{\equiv}CH + 4Na \longrightarrow 4NaC_2H + CH_3CH_3 \quad (6 + 11)$$

The further attack of $Na^+[NH_3]\cdot^-$ on ethylene *via* the second-stage mechanism (steps 7–10) is a minor route compared to the first stage. The amount of ethane experimentally observed (gas chromatography) averages only one-eighth the amount of ethylene produced (Tables II and III).

However, the fact that in the absence of ammonia, ethylene and ethane are still obtained indicates that electron transfer is still possible *via* the direct reaction of sodium with liquid acetylene to yield ion radical I. The rate of this reaction, however, is much slower than that observed with the sodium–ammonia species $[Na^+\text{-}NH_3]\cdot^-$, but steps 2–5 are still possible.

$$Na\cdot + CH{\equiv}CH \longrightarrow \underset{I}{Na^+[\dot{C}H{=}\ddot{C}H]^-}$$

The possible formation of butadiene *via* the dimerization of the acetylene anion radical $\dot{C}H{=}\ddot{C}H^-$ is believed to be an insignificant reaction due to the 99% material balance realized for products such as NaC_2H, ethylene and ethane (steps 1–11). Also its presence was not noted by gas chromatography.

The above mechanism is actually a simplification of a much more complicated solvation process. Both liquid acetylene and ammonia, mutually complexed (H bonded),[10] probably function together to complex and activate such species as $NH_3\cdot^-$, Na^+, $^-\cdot[CH{=}\ddot{C}H]$, $[CH_2{=}\ddot{C}H]$, thereby facilitating the entire reaction sequence. Also, the reaction of III with acetylene (step 5) probably involves the transfer of H^+ from acetylene to III. This could be accomplished by the ionization of a C_2H_2–NH_3 complex or by NH_4^+ derived from the complex. The latter possibility is shown in Scheme I.

SCHEME I

$$C_2H_2 + NH_3 = C_2H_2\cdot NH_3 = C_2H^- + NH_4^+$$

$$\underset{III}{[CH_2{=}\ddot{C}H]^-Na^+} + C_2H^- = NaC_2H + [CH_2{=}\ddot{C}H]^-$$

$$[CH_2{=}\ddot{C}H]^- + NH_4^+ \longrightarrow NH_3 + CH_2{=}CH_2$$

The large amount of hydrogen formed in organic solvents compared to its absence in liquid acetylene in turn indicates the former process involves intermediate radical (H·) formation besides proton transfer. Acetylide formation in organic media is a complicated surface process[15] involving a number of intermediate color changes. Alkali metal dispersions are mandatory, and at no time in the process is a homogenous solution observed. The ready formation of atomic and eventually molecular hydrogen from such active surfaces in organic solvents is believed more likely than in a homogenous liquid acetylene system where even KOH is dissolved[10] by complex formation.

TABLE IV

SODIUM PROPIOLATE FORMATION[a]

Expt no.	Na, g-atom	C_2H_2, mol	CO_2, mol	Cocatalyst, mol	Temp, °C	% conversion
1	0.18	0.90	0.50	0.05[b]	5–23	85
2	0.18	0.90	0.50	0	4–21	34
3	0.075[c]	0.80	0.28	0	−25–15	57
4	0.075[c]	0.40	0.28	0.49[d]	−8–27	55
5	0.18	0.90	0.50	0.05[e]	−9–20	10

[a] All runs used a 2-hr reaction time except expt 3 (1.25 hr). Average pressure range was 300–630 psig (−9 to 27°). [b] Trimethylamine. [c] Sodium acetylide used in place of sodium. [d] Dioxane. [d] Ammonia.

Carbonation of Sodium Acetylide to Sodium Propiolate.—A simple, one-step method for the preparation of sodium propiolate by the interaction of sodium, liquid acetylene and liquid carbon dioxide in the presence of a small amount of trimethylamine (TMA) has been developed.

$$Na + CH{\equiv}CH \xrightarrow{TMA} HC{\equiv}CNa$$

$$Na{-}C{\equiv}CH + CO_2 \longrightarrow HC{\equiv}CCO_2Na$$

The reaction takes place (Table IV, expt 1) under mild conditions (5–23°) during a 2-hr period to give an 85% conversion to sodium propiolate. Sodium and excess liquid acetylene are allowed to react for approximately 30 min in the presence of the cocatalyst, trimethylamine, before introducing liquid carbon dioxide.

Previous methods[19,20] involved the preformation of sodium acetylide in organic solvents (xylene, DMF, dioxane, etc.) or liquid ammonia. Acetylide prepared in organic solvents requires temperatures from 75 to 140°, while the use of liquid ammonia dictates the later removal of ammonia and the use of a substitute solvent before carbonation; otherwise, ammonium carbamate formation predominates. The sodium acetylide–solvent slurry is then transferred to an autoclave for carbonation with gaseous CO_2. Acetylide formed at elevated temperatures is less active, and is often contaminated with sodium carbide (Na_2C_2), which is either converted into by-product acetylenedisodium carboxylate ($CO_2NaC{\equiv}CCO_2Na$) or may be responsible for pyrophoric samples of sodium propiolate obtained when exposed to the atmosphere.

Table IV also shows that in the absence of trimethylamine only a 34–57% conversion is realized (expt 2 and 3), while the use of dioxane as cocatalyst (expt 4) gives no significant improvement (55%) in conversion. Ammonia (expt 5) was actually detrimental to the carbonation (10% conversion) owing to ammonium carbamate formation.

The interaction of liquid CO_2 and trimethylamine (TMA) under pressure at 5–20° was observed to yield a solid complex which decomposed as the pressure was released (*cf.* Experimental Section). This intermediate

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(19) L. N. Owen, *et al.*, *J. Chem. Soc.*, **3**, 111 (1949).

(20) A. N. Kurtz, (to Union Carbide Corp.), U. S. Patent 3,211,662 (1963); Belgian Patent 63,6771 (1963).

TMA–CO_2 complex (probably soluble in liquid acetylene) may be an activated species involved in the rapid, low-temperature carbonation of sodium acetylide.

Experimental Section

Apparatus.—A reaction system for safely liquefying and handling acetylene was described previously.[10] The reactor used in the following experiments was a 125-cc stirred autoclave equipped with jacketed walls through which a heat exchange fluid (methanol) was circulated to control the reactor temperature.

Acetylene was added to the autoclave (usually at −30 to 0°) from a calibrated buret after assembling and pressure testing the equipment. Other materials (gases, liquefied gases, liquids) were introduced *via* standard techniques from pressure burets also calibrated and equipped with needle valves allowing accurate control of addition rates and quantities of materials added.

Solids, slurries, etc., were charged into the autoclave before assembling. In all cases the autoclave and the entire pressure system were purged with N_2 and dried thoroughly before each run. The heating–cooling system has already been described.[10]

Preparation of Alkali Metal Acetylides in Liquid Acetylene.—Acetylene was added to the alkali metal (dispersion in light mineral oil, or a freshly prepared sand in xylene) at various temperatures and pressures as shown in Table I. At −5°, the desired amount (by volume) of liquid ammonia was added (5–10 min). The mixture was allowed to warm gradually, until a mildly exothermic reaction occurred raising the reaction temperature to about 17°. Cooling for approximately 2 min was sometimes necessary to hold the temperature below 20°. The mixture was stirred from 1.25 to 5.5 hr during which time it slowly warmed to room temperature.

Hexane (50 ml) was introduced followed by slowly bleeding off the gases. The hexane slurry was removed, and the mixture centrifuged to separate hexane from the acetylide. Unnecessary exposure of the product to air and moisture was avoided during the isolation step. The solid was washed with hexane, followed by drying at room temperature in a vacuum desiccator. Products were analyzed for total alkali metal and acetylenic hydrogen content by well-known procedures.[21]

Reaction of Sodium and Acetylene in the Presence of Ammonia and Analysis of the Gases Bled Off.—The procedure described above for the preparation of sodium acetylide in the presence of ammonia was followed. Sodium dispersion (0.2 g-atom), liquid acetylene (0.9 mol) and ammonia (0.05 mol) were stirred 3 hr at 11–25° (540–692 psig). During this time gas samples were taken and analyzed by gc (20% dimethylsulfolane on Gas-Chrom-R) for ethane, ethylene and acetylene (see Table II). Retention times at ice–water temperature were ethane, 5 min; ethylene, 5.5 min; acetylene, 12 min. Hydrogen content was checked by gc using a column packed with 5A Molecular Sieves at room temperature (retention time 1 min).

A run was carried out reacting sodium (0.2 g-atom), acetylene (0.90 mol) and ammonia (0.05 mol) for 0.5 hr at 5–30° (610–745 psig). The entire gas content was collected in a 32.8-l. tank and analyzed by gc (see Table III, run A).

A run was carried out reacting sodium (0.10 g-atom) and acetylene (0.45 mol), in the absence of ammonia, for 5.5 hr at 21–26° (520–560 psig). The entire gas content was collected in a 32.8-l. tank and analyzed by gc (see Table III, run B).

Formation of Sodium Propiolate Starting with Sodium Dispersion in the Presence of Trimethylamine.—Sodium dispersion (12 cc, 0.178 g-atom, 40% in mineral oil), acetylene (45 cc, 0.9 mol), and trimethylamine (4.7 cc, 0.05 mol) were warmed from −5° to room temperature and stirred 0.5 hr. Occasional cooling was necessary to maintain room temperature. At 2–12° liquid CO_2 (37 cc, 0.5 mol) was added over a 15-min period. The mixture was stirred 2 hr during which time the temperature rose slowly to 23°.

The gases were bled off. The solid was washed with hexane to remove the small quantity of mineral oil, then dried in a vacuum oven at 40°. The weight of finely divided, light brown powder was 15.1 g. By analysis it contained 27.2% total sodium, 92.3% sodium propiolate and 4.4% sodium acetylide. No free sodium was detected. Conversions, based on total sodium, to sodium propiolate and sodium acetylide were 84.7 and 7.3%, respectively.

In the Absence of Ammonia or Trimethylamine.—Sodium dispersion (12 cc, 0.19 g-atom) and liquid acetylene (45 cc, 0.9 mol) were stirred 0.5 hr at room temperature. At 5–10° liquid carbon dioxide (37 cc, 0.5 mol) was added over a 0.5-hr period. The mixture was stirred 2 hr allowing the temperature to increase slowly to 21°.

The solid product was washed with hexane and pumped dry (weight 13.4 g). Free sodium was present because sparks could be seen when a small quantity of the solid was sprinkled on water. The solid contained 32.7% total sodium (partly as free metal), 11.8% sodium acetylide and 47.8% sodium propiolate. Based on total sodium the conversions to sodium acetylide and sodium propiolate were 17.3 and 33.7%, respectively.

Carbonation of Sodium Acetylide in Liquid Acetylene.—Sodium acetylide (79% pure, 3.6 g, 0.059 mol) was placed in the autoclave followed by closing and pressure testing with N_2. At −40° liquid acetylene was added (40 cc, 0.8 mol). Over a period of 15 min and at −25° liquid carbon dioxide (30 cc, 0.4 mol) was added. The mixture was stirred 1.25 hr at 8–15°, followed by bleeding off the gases.

The solid product weighed 5.8 g and contained 54% sodium propiolate and 4.5% unreacted sodium acetylide. The conversion to sodium propiolate, based on sodium acetylide used, was 57%. The recovery of sodium acetylide was 10.0%.

Registry No.—Acetylene, 74-86-2.

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[21] L. Barnes, Jr., and L. J. Molinini, *Anal. Chem.*, **27**, 1025 (1955).