it was allowed to stand for 48 hr. at room temperature. A blank was also prepared. A color change from blue to green indicated that reaction had taken place. An additional check was provided by analysis for Cr^{++} and comparison with the blank.

The Rate of Mercuration of Benzene as a Function of the Activity of Water

BY CHARLES PERRIN[1a] AND F. H. WESTHEIMER[1b]

Earlier research had shown that neutral salts strongly accelerate the mercuration of benzene in dilute aqueous acid; the present work shows that 7.5 M sodium perchlorate increases the rate 300-fold. The reaction is not acid-catalyzed; the acceleration is not an effect of the salts on the acidity functions H_0 or H_R but rather is caused by the progressive removal of water from the mercuric ion. This conclusion is based upon the correlation between the rate of mercuration and the vapor pressure of water above the solutions; the second-order rate constant is an inverse monotonic function of a_{H_2O}. A function Hg_0 describes the activation of Hg^{++} as water is withdrawn from it, much as H_0 describes the activation of H^+ under like conditions. The primary deuterium isotope effect is large, so the mechanism of mercuration involves rate-limiting deprotonation of $C_6H_5HHg^{++}$. The kinetics are complicated by extensive polymercuration; σ^+ for the Hg(II) substituent is only about 0.1. The relative rates of mono-, di-, and trimercuration were estimated from product analyses, and the system of kinetic equations was solved with the aid of an analog computer.
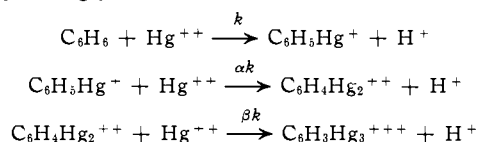
Introduction

The mercuration of benzene with mercuric perchlorate in aqueous solution is strongly accelerated by the addition of perchloric acid or of its neutral salts[2–4]; the present work shows that 7.5 M sodium perchlorate increases the rate in the presence of 0.5 M perchloric acid by a factor of 300. The rates are large compared to those for mercuration with the complexes of mercuric ion, such as the acetate. The acceleration by salts had previously[3] been ascribed to the formation of a reactive mercuric perchlorate complex, or alternatively[5] to a partially dehydrated mercuric ion which might be formed in the solution as the ions of the neutral salt, because of their own hydration, reduced the availability of water. But prior to the present work, the mode of action of salts was suspect. All the mercuration reactions are necessarily conducted in the presence of a small amount of mineral acid, since otherwise mercuric ion undergoes hydrolysis to form $Hg(OH)^+$, or to precipitate the oxide from solution. Further, neutral salts have a pronounced effect upon the acidity functions[6,7] of the solvent; our own work shows that 7.3 M $NaClO_4$ makes the H_0 value of 0.5 M $HClO_4$ 1.8 units more negative, and 6.3 M $NaClO_4$ makes the H_R value of 1.57 M $HClO_4$ 2.8 units more negative. Therefore the effect of neutral salts might have proved to be only that of lowering H_0 (or some alternative acidity function), mercuration would then be acid-catalyzed. This idea has proved incorrect; our findings show that the rate of mercuration is not affected by acidity *per se*, but is an inverse function of the activity of water in the solution.
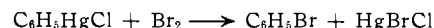
The kinetics of the mercuration of benzene was followed by titration of the reaction mixture with thiocyanate; Hg^{++} requires two equivalents, whereas arylmercuric ions require but one for each equivalent of bound mercury(II). The reactions were generally carried out in the presence of a large excess of benzene, so that the aqueous solutions remained saturated.

Thus in any experiment, the concentration of benzene was constant, whereas that of the phenylmercuric ion increased with time. Under our experimental conditions, phenylmercuric ion is further mercurated; the positively charged mercuric ion does not deactivate the ring strongly.

$$C_6H_6 + Hg^{++} \xrightarrow{k} C_6H_5Hg^+ + H^+$$

$$C_6H_5Hg^+ + Hg^{++} \xrightarrow{\alpha k} C_6H_4Hg_2^{++} + H^+$$

$$C_6H_4Hg_2^{++} + Hg^{++} \xrightarrow{\beta k} C_6H_3Hg_3^{+++} + H^+$$

The composition of the mixed product was obtained by converting the mercurated benzenes to bromobenzenes; *e.g.*

$$C_6H_5HgCl + Br_2 \longrightarrow C_6H_5Br + HgBrCl$$

The bromobenzenes were then analyzed by vapor-phase chromatography and infrared spectroscopy.

The chemical equations above lead to a complicated set of differential equations, which were handled with the aid of an analog computer. The solubilities of benzene were determined for enough solutions to allow an estimate of the concentration under each set of experimental conditions. The H_0 and H_R values of the solutions and their vapor pressures were measured, and the rates of mercuration compared with each of these functions.

Experimental

Materials.—Fisher Certified ACS benzene (thiophene-free[8]) was used without further purification. Benzene-d_6 was obtained from Merck of Canada, Ltd. Reagent grade perchloric acid (B & A, J. T. Baker, and Merck) was standardized against Merck Reagent sodium borate. Fischer purified sodium perchlorate monohydrate was recrystallized from water and dried to the anhydrous salt *in vacuo* at 95°; it contained less than 0.01% chloride. Anhydrous lithium perchlorate (Foote Mineral Co.) was twice recrystallized from water and vacuum dried, first at 95° and then at 140°. Solutions of mercuric perchlorate were prepared by dissolving yellow mercuric oxide (Mallinckrodt A.R.) in excess perchloric acid (with or without added salt) and filtering through a sintered glass funnel. Standard solutions of mercuric nitrate were prepared from triple-distilled mercury and nitric acid. Standard solutions of potassium thiocyanate were made up by weight from dried Mallinckrodt A.R. material. Bromobenzene, *o*-, *m*-, and *p*-dibromobenzene, and *sym*-tribromobenzene were Eastman White Label products, purified when required. 1,2,4-Tribromobenzene was prepared by the bromination of *p*-dibromobenzene in the presence of ferric and aluminum chlorides; the final product (m.p. 37–38°, lit. value[9] 43°) was better than 99% pure, as estimated by vapor-phase

(1) (a) National Science Foundation Cooperative Fellow, 1960–1962; (b) John Simon Guggenheim Fellow, 1962–1963.

(2) F. H. Westheimer, E. Segel, and R. M. Schramm, *J. Am. Chem. Soc.*, **69**, 773 (1947).

(3) R. M. Schramm, W. Klapproth, and F. H. Westheimer, *J. Phys. Colloid Chem.*, **55**, 843 (1951).

(4) W. J. Klapproth, Ph.D. Thesis, University of Chicago, 1949.

(5) F. H. Westheimer, personal communication to C. K. Ingold, as quoted in C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 305.

(6) G. Harbottle, *J. Am. Chem. Soc.*, **73**, 4024 (1951).

(7) M. A. Paul and F. A. Long, *Chem. Rev.*, **57**, 1 (1957).

(8) H. N. Holmes and N. Beeman, *Ind. Eng. Chem.*, **26**, 172 (1934).

(9) C. Wurster, *Ber.*, **6**, 1490 (1873).

TABLE I
TRIARYLCARBINOLS

Substituents	Synthesis	Wt. % H_2SO_4 for extraction	M.p., °C. (lit. m.p.)
p,p'-Dimethoxy	$C_6H_5Li + (p\text{-}CH_3OC_6H_4)_2CO$	45	73.9-75.0 (76-77[11])
p-Methoxy	$C_6H_5MgBr + p\text{-}CH_3OC_6H_4CO_2CH_3$	65	60.6-61.6 (58-61[12])
p-Methyl	$p\text{-}CH_3C_6H_4MgBr + (C_6H_5)_2CO$	75	71.8-72.9 (73-74[13])
p,p',p''-Trichloro	$p\text{-}ClC_6H_4MgBr + (p\text{-}ClC_6H_4)_2CO$	80	96.1-96.7 (98-99[14])

chromatography. o- and p-nitroaniline were purified by Dr. Ronald Cieciuch.[10] Eastman Practical grade 4-chloro-2-nitroaniline was recrystallized from water; m.p. 116-117°.

Triarylcarbinols.—The purification and crystallization of substituted triarylcarbinols have been a source of difficulties for many investigators. These compounds may, however, be successfully purified by taking advantage of their indicator properties, i.e., by extracting them from benzene with sulfuric acid of the strength reported in Table I.

Methods. (a) Reaction Kinetics.—Mercurations were carried out at 39.96 + 0.02° in 100-ml. three-necked ℥ r.b. flasks; the contents were stirred with a Teflon paddle sealed with silicone grease. To minimize volatilization of benzene-d_6, isotope effects were determined in stoppered 25-ml. flasks, equipped with magnetic stirrer. In each case, the extent of mercuration was determined by titration for mercuric ion. A 1-ml. sample of the mercurating solution was withdrawn with a calibrated Krogh-Keyes syringe pipet and was added to excess potassium thiocyanate solution, measured with a 5-ml. hypodermic syringe and calibrated Traylor slug.[15] The excess thiocyanate was back titrated below 10° with standard 0.05 M mercuric nitrate solution, using ferric nitrate as indicator. The reactions were started by the addition of benzene, and the mixture vigorously stirred except during the short periods when samples for analysis were removed. In general, eight to ten points were taken over 40-50% of complete consumption of the mercuric ion. Precipitation of product occurs with high-salt, low-acid solutions, so such reactions were carried to only 8-30% completion. For fear of depleting the organic layer, reactions with benzene-d_6 were carried to only 20-40% completion, with slight loss of precision.

Previous work[16] had shown that the reaction is second order (first order in benzene and first order in mercuric ion). In particular, the rate is independent of the volume of the benzene layer above the aqueous solution, or of the rate of stirring. The reaction therefore occurs in the aqueous layer. Furthermore, the second-order rate constants obtained with dilute homogeneous solutions of benzene agree with those observed with saturated solutions of benzene in aqueous perchlorate mixtures.

(b) Analog Computation.—Rate constants were fitted to the experimental data with a PACE electronic analog computer equipped with a Servomultiplier and a Variplotter (Electronic Associates, Inc.). The experimental points (fraction mercuration vs. time) were plotted on 15 in. × 10 in. graph paper. By adjusting one potentiometer on the PACE electronic analog computer, so as to cause the machine tracing to follow the experimental points, the first-order rate constant for each run was determined (see Mathematical Appendix).

(c) Determination of the Solubility of Benzene.—The molar extinction coefficient of benzene at 40° was found as 160 ± 5 at 2538 Å. with a Zeiss PMQ II spectrophotometer. To determine the solubility of benzene, enough of a particular perchlorate solution was added to a 1-cm. cell to cover the optical face of an 0.8-cm. quartz insert. Excess benzene was added, and the cell closed with a Teflon plug. The cell was shaken vigorously, and allowed to equilibrate at 40° in the thermostated cell block. Every half hour, the optical density was read, the cell shaken again, and replaced. Equilibration was slow, requiring hours. Care was taken to avoid errors from either droplets of benzene on the optical faces or vapor in the optical path. The precision of the solubility measurements was ±4%.

The solubilities of benzene in 24 different perchlorate solutions were determined and plotted[17] as contours of equal solubility. The function which represents the solubility measurements is extraordinarily complicated. Nevertheless, the solubility of benzene in each mercurating solution was obtained by linear interpolation, with care to avoid interpolation through regions of convolution of contour lines. These solubilities are listed with the corresponding rate constants of Table III and are probably correct to ±5%. Nevertheless, the greatest source of error in

(10) R. F. W. Cieciuch, Ph.D. Thesis, Harvard University, 1960.

(11) A. Baeyer and V. Villiger, Ber., **36**, 2787 (1903).

(12) A. Baeyer and V. Villiger, ibid., **35**, 3027 (1902).

(13) S. F. Acree, ibid., **37**, 992 (1904).

(14) A. Baeyer, ibid., **38**, 586 (1905).

(15) T. G. Traylor and R. A. Crane, Experientia, **17**, 35 (1961).

(16) R. M. Schramm, Ph.D. Thesis, University of Chicago, 1947.

(17) C. Perrin, Ph.D. Thesis, Harvard University, 1963; Dissertation Abstr., XXIV, Issue 5, No. 63-7835 (1963).

TABLE II
ISOPIESTIC SOLUTIONS AT 40°

M HClO$_4$	M NaClO$_4$	M HClO$_4$ +	M NaClO$_4$
2.432	3.118	1.172	1.570
5.161	7.575	2.720	3.536
5.157	7.555	2.736	3.547
6.400	9.745	3.162	4.985
2.362	2.989		
3.072	3.958		
4.582	6.561		

TABLE III
RATES OF MERCURATION AT 40°

Reaction solution		Solubility of benzene, mM	$-\log a_{H_2O}$	k_2, l./mole min.	$-Hg_0 - \log (Hg^{++})$
M HClO$_4$	M NaClO$_4$				
0.397	..	30.3	0.006	2.21×10^{-3}	0.12
.0054	3.00	17.8	.055	1.25×10^{-2}	.87
.508	2.50	19.8	.060	1.33×10^{-2}	.89
2.795	..	37.5	.072	1.64×10^{-2}	.98
3.45	..	39.3	.103	3.01×10^{-2}	1.25
2.00	2.00	23.5	.106	3.63×10^{-2}	1.33
0.506	4.00	13.9	.106	4.54×10^{-2}	1.43
4.31	..	41.8	.157	8.20×10^{-2}	1.68
0.081	6.01	8.23	.159	1.9×10^{-1}	2.05
2.34	3.00	17.2	.168	1.60×10^{-1}	1.97
0.606	5.50	9.35	.170	1.75×10^{-1}	2.01
2.03	3.00 (Li$^+$)	24.5	.203	2.28×10^{-1}	2.13
4.04	2.00	25.1	.259	4.43×10^{-1}	2.42
0.443	7.51	6.67	.271	7.5×10^{-1}	2.65
3.04	4.00	17.0	.296	6.00×10^{-1}	2.55
5.97	..	38.6	.327	9.00×10^{-1}	2.72
2.415	6.00	12.0	.388	1.70	3.00
6.65	..	37.6	.436	2.47	3.16
6.91	..	37.1	.481	3.84	3.35
4.415	4.00	29.8	.491	2.93	3.24
5.86	2.00	24.6	.528	5.20	3.49

the second-order rate constants may lie in the inaccuracy of these solubility measurements.

(d) Vapor pressure determinations were made at 40° in an apparatus adapted from Scatchard[18] and from Mason.[19] Since the vapor pressures of solutions of perchloric acid alone[20] and those of sodium perchlorate alone were here determined,[21] the experiments led to the determination of acid-salt mixtures isopiestic with the solutions of the acid alone, or of the salt alone. These compositions are presented in Table II.

A great economy in measurement resulted from the observation that the isopiestic contours are nearly straight lines in the M HClO$_4$–M NaClO$_4$ plane.[17] The set of isopiestic solutions listed in Table II was used to evaluate the molarity of sodium perchlorate equivalent to (isopiestic with) the molarity of perchloric acid. The vapor pressure of each solution used was determined by comparison with these curves. The values used for each mercurating solution are listed, along with the rate constants in Table III.

A linear relation for vapor pressure of mixtures of perchloric acid and lithium perchlorate was assumed in order to determine the molarity of a perchloric acid solution isopiestic to the single perchloric acid–lithium perchlorate mercurating solution. The

(18) G. Scatchard, W. J. Hamer, and S. E. Wood, J. Am. Chem. Soc., **60**, 3061 (1938).

(19) C. M. Mason and H. M. Gardner, J. Chem. Educ., **13**, 188 (1936).

(20) J. F. Bunnett, J. Am. Chem. Soc., **83**, 4967 (1961).

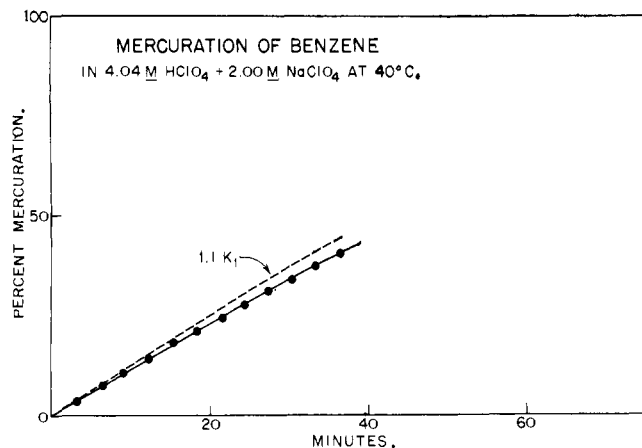(21) The values of J. H. Jones (J. Phys. Colloid. Chem., **51**, 516 (1947)) were at 25°.

Fig. 1.—The mercuration of benzene. Percentage mercuration is plotted against time in minutes, and the curve through the experimental points was obtained with the analog computer. The precision of the determination of k is shown.

needed vapor pressures of the solutions of lithium perchlorate and perchloric acid were from the data of Jones,[21] and of Robinson and Baker[22]; the densities are from the "International Critical Tables."

(e) **Ratios of Polymercurated Species.**—The mercurated products were precipitated with aqueous sodium chloride solution as the chlorides, and then converted to the corresponding bromobenzenes by the method of Dimroth[23]; no isomerization accompanies this procedure.[24] The ratios of bromobenzene to dibromobenzenes to tribromobenzenes were determined with an Aerograph gas chromatographic instrument and a Varian G-10 recorder. Sufficient samples were collected for infrared analysis. Comparison of the spectra with spectra of known mixtures of o-, m-, and p-dibromobenzenes showed that comparable quantities of the three isomers are produced.

Results

Acidity Functions.—The values of pK_A and pK_R for the indicators were determined[17] at 40° by the methods of Hammett[7,25] and of Deno.[26] The absolute values of the two acidity scales were set by assigning a pK_A of 0.99 to p-nitroaniline and a pK_R of -1.14 to bis-(p-methoxy)-triphenylcarbinol. Some of the pK's differ from those of Deno by 0.4 pK unit. Perhaps the differences are in part caused by a large temperature dependence[27] of ΔpK. However, even if the pK's are somewhat in error, acidities determined with any given indicator will be internally consistent.

The acidity values were obtained at 40° for perchloric acid solutions, for perchloric acid–sodium perchlorate mixtures, and for perchloric acid–lithium perchlorate mixtures; detailed tables of these data are available elsewhere.[17] Although most of these values represent single measurements, they served for the construction of contours of constant acidity; interpolation served to determine H_0 and H_R values at 40° for the mercurating solutions (see Fig. 3–5). For those reactions in very low initial acid concentration, the hydrogen ion concentration was chosen as that present half-way through the kinetic run. Even with the one experiment begun with only 0.005 M acid, the hydrogen ion concentration at 50% mercuration (when the reaction was stopped) was less than double the value chosen, or less than 0.3 logarithmic unit more acid.

(22) R. A. Robinson and O. J. Baker, *Trans. Proc. Roy. Soc. New Zealand*, **76**, 250 (1946).

(23) O. Dimroth, *Ann.*, **446**, 148 (1926).

(24) M. S. Kharasch and L. Chalkley, *J. Am. Chem. Soc.*, **43**, 607 (1921).

(25) L. P. Han mett and A. Deyrup, *ibid.*, **54**, 2721 (1932).

(26) N. C. Deno, H. E. Berkheimer, W. L. Evans, and H. J. Peterson, *ibid.*, **81**, 2344 (1959).

(27) N. C. Deno, J. J. Jaruzelski, and A. Schriesheim, *ibid.*, **77**, 3045 (1955); see, however, R. Stewart and T. Mathews, *Can. J. Chem.*, **38**, 602 (1960).
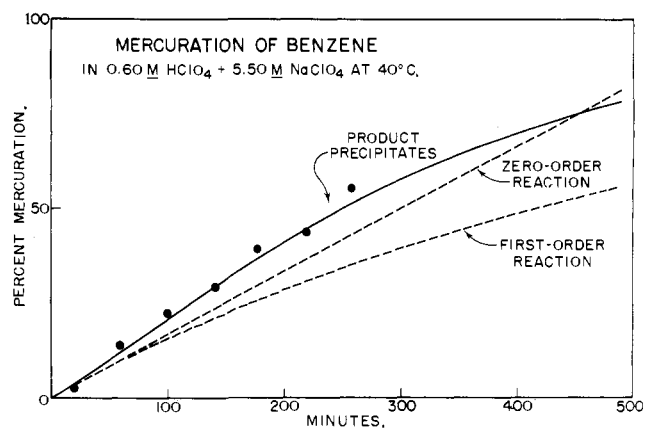
Fig. 2.—The mercuration of benzene. Percentage mercuration is plotted against time in minutes, and the curve through the experimental points was obtained with the analog computer.

With all other solutions, the uncertainty in acidity was negligible.

Rates of Mercuration.—The second-order rate constants for mercuration are listed in Table III. Specially selected values of the rate constants, which contrast the effects of sodium perchlorate and perchloric acid, are assembled in Table IV. The rates of mercuration of benzene-d_6, as compared to those for benzene, are listed in Table V.

TABLE IV

SELECTED VALUES OF RATES OF MERCURATION AT 40° COMPARED TO H_0 AND H_R

M HClO$_4$	M NaClO$_4$	$-H_0$	$-H_R$	$3 + \log k_2$
0.397	. .	-0.33	0.31	0.345
.0141	3.00	-1.30	0.10	1.10
.5085	2.50	0.38	1.83	1.124
2.795	. .	1.06	2.82	1.214
0.083	6.01	0.52	2.27	2.28
3.45	. .	1.37	3.47	1.478
4.31	. .	1.77	4.26	1.914
0.443	7.51	1.54	3.45	2.89

TABLE V

ISOTOPE EFFECTS IN MERCURATION

Reaction solution		
M HClO$_4$	M NaClO$_4$	$k_{C_6H_6}/k_{C_6D_6}$
0.397	. .	6.75
4.04	2.00	5.62
6.65	. .	4.68

Figure 1 illustrates the precision of the curve-fitting; the dashed line corresponds to a rate constant 10% greater than that obtained for the solid curve. Figure 2 shows the results of an experiment carried near to completion. The odd shape of the curve, nearer to zero than to first-order reaction, arises as an effect of the polymercuration. Obviously, the curves drawn by the analog computer fit the complicated set of differential equations well; the rate constants are reliable to a few per cent. Furthermore, the solution of the equations is not sharply influenced by the values of α and β employed in the calculation. (These are the ratios of the rate constants for di- and trimercuration to that for monomercuration; they are not arbitrary parameters, but are obtained from experiment as outlined below.)

Polymercuration.—The ratios of mono-, di-, and tribromobenzenes, as determined by v.p.c. for each of five reaction mixtures, are listed in Table VI. The columns headed mono, di, and tri list the ratios of products, "normalized" to r, the ratio of the initial concentration of mercuric ion to the molar solubility of benzene.
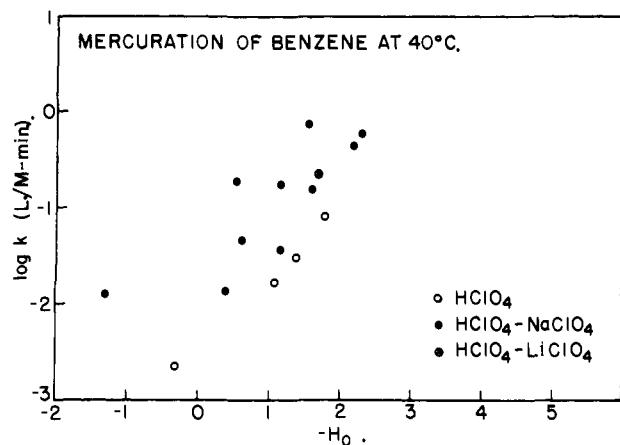
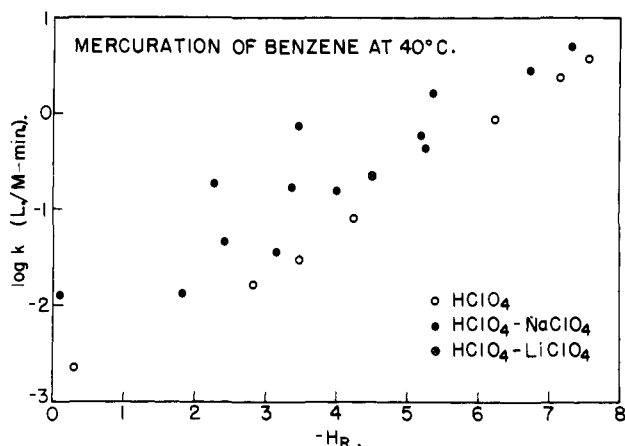Fig. 3.—The logarithm of the rate constant for mercuration plotted against $-H_0$.

Fig. 4.—The logarithm of the rate constant for mercuration plotted against $-H_R$.

The parameters α and β are the ratios of the rate constants for dimercuration and trimercuration to that for monomercuration. The determination of these parameters (to about $\pm 10\%$) from the analytical data for the bromobenzenes is explained in the Mathematical Appendix. Values of α and β for mercurating solutions were interpolated from the data of Table VI on the assumption that they are functions only of the vapor pressure of water.

TABLE VI

RATE CONSTANT RATIOS FOR POLYMERCURATION

Reaction solution			"Normalized" product ratios			Rate constant ratios	
M HClO$_4$	M NaClO$_4$	$(\text{Hg}^{++})_0/ S_{\text{benzene}}$	Mono	Di	Tri-	α	β
2.795		5.84	2.18	1.45	0.25	0.37	0.13
4.04	2.00	8.81	3.60	2.34	.175	.216	.037
5.97		5.66	3.25	1.155	.031	.167	.019
5.86	2.00	8.89	4.39	2.13	. . .	.15	. . .
6.91		5.91	3.48	1.18	0.019	.15	0.011

Discussion

Rates of Mercuration.—The rates of mercuration are compared below (a) with the total perchlorate ion concentration, (b) with H_0 and H_R, (c) with H_{++} and H_{R++}, and, finally, (d) with the logarithm of the activity of water.

(a) **Rates of Mercuration and Total Perchlorate Ion Concentration.**—Although the correlation in solutions up to about 1 M is quite good,[3] in more concentrated solutions the correlation between rate constants and total perchlorate ion concentration is poor. For example, the reaction in ₃.65 M perchloric acid is 45% faster than that in 2.42 M perchloric acid plus 6.0 M
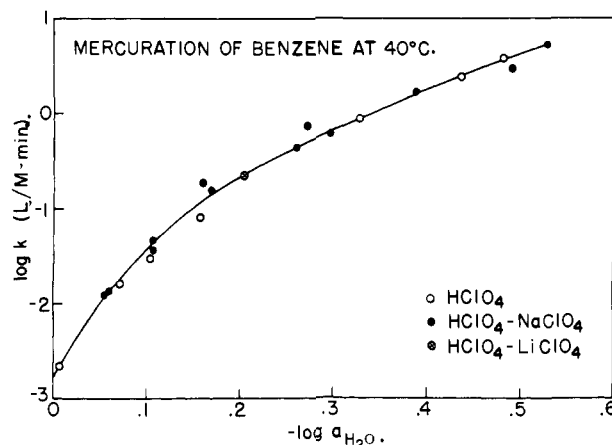

Fig. 5.—The logarithm of the rate constant for mercuration plotted against the negative logarithm of the activity of water.

sodium perchlorate, despite the much higher total perchlorate content of the latter reaction mixture. Additional examples can be selected from the data of Table III. Significantly, in concentrated solutions, perchloric acid is consistently a better catalyst than an equal concentration of sodium perchlorate.

(b) **Rates of Mercuration and H_0 and H_R.**—If the rate of reaction were controlled by H_0, then the Hammett–Deyrup equation[25,28,29] would apply; that is, $\log k + H_0 = $ a constant. A similar relationship would hold for H_R if this were the kinetically significant function. The failure of such relationships is shown in Fig. 3 and 4, and is highlighted in the selected data of Table IV. For example, the first two lines of Table IV contrast the rate of reaction in a solution containing 0.397 M perchloric acid with that in a solution containing 0.0141 M perchloric acid plus 3.00 M sodium perchlorate. The rate of reaction in the solution with sodium perchlorate is about six times as great as that in the solution without salt, yet the H_0 value for the first solution is nearly a full unit more negative; the total discrepancy between rate and H_0 is nearly a factor of 60. The difference is not so great for H_R, but here the discrepancy is nearly a factor of 10. Similar comparisons can be made with other matched pairs. Thus the data unambiguously demonstrate that mercuration, under these experimental conditions, is not acid-catalyzed. (Acid catalysis for mercuration with mercuric acetate in acetic acid solution is well understood[3]; it depends on freeing mercuric ion from its complex with acetate ion.) Sodium perchlorate is consistently a better catalyst than could be anticipated from its effect upon acidity.

(c) **Rates of Mercuration and H_{++} and H_{R++}.**—Ideally, rates should have been compared with the acidity functions H_{++} and H_{R++} rather than H_0 and H_R. However, H_+[7,30] (and therefore presumably H_{++}) probably does not differ very much from H_0. Furthermore, cationic indicators of the triarylcarbinol series have been studied in sulfuric acid solution.[31] Their change in color with change in the concentration of acid closely parallels that for the uncharged indicator. tri-(p-nitrophenyl)-carbinol[32]; H_{R++} therefore parallels H_R, and nitration[33] of $C_6H_5N(CH_3)_3^+$ similarly paral-

(28) L. Zucker and L. P. Hammett, *J. Am. Chem. Soc.*, **61**, 2791 (1939).

(29) F. A. Long and M. Paul, *Chem. Rev.*, **57**, 935 (1957).

(30) J. C. D. Brand, W. C. Horning, and M. B. Thornley, *J. Chem. Soc.*, 1374 (1952).

(31) A. M. Lowen, M. A. Murray, and G. Williams, *ibid.*, 3318 (1950).

(32) F. H. Westheimer and M. Kharasch, *J. Am. Chem. Soc.*, **68**, 1871 (1946).

(33) T. G. Bonner, F. Bowyer, and G. Williams, *J. Chem. Soc.*, 3274 (1952).

lels H_R. Therefore the use of H_0 and H_R is unlikely to introduce important errors into our treatment. At the least, the qualitative conclusions should be valid.

Theory, too, supports the argument that H_0 and H_R may be used in place of H_{++} and H_{R++} in the present instance. By analogy with the model of Bascombe and Bell,[34] $-H_{++}$ will be equal to log (H^+) minus some undetermined function of the activity of water. Such a relationship will prevent rates from being correlated with H_{++}, just as it prevents correlation with H_0 or H_R.

(d) **Rates of Mercuration and Water Activity.**— Figure 5 shows that the second-order rate constants for mercuration correlate quite well with the activity of water in the solutions. Deviations from the curve are greater than experimental error but nevertheless small enough to be caused by specific salt effects superimposed upon a larger dehydration effect.

The initial slope of the plot of log k against the log of the activity of water is about 15, as contrasted to about 10 for the corresponding[20,35] plot for H_0. The slope decreases to about 4 in the most concentrated solutions studied (8 M). In similar fashion to the general line of argument for H_0 discussed by Bascombe and Bell,[34] by Wyatt,[35] and by Bunnett,[20] the slope of the curve can be qualitatively identified with the release of water from the mercuric ion in the transition state.

Mercuration then is one of a number of reactions where water acts as a strong inhibitor by solvating an essential cation. Qualitatively similar effects have been noted for the inactivation of anions by water.[36,37]

The Hg_0 Function.—By analogy with the H_0 function, the Hg_0 function may be defined by the thermodynamic equation

$$Hg_0 = -\log hg_0 = -\log a_{Hg^{++}}f_S/f_{SHg^{++}}$$

where S is an aromatic hydrocarbon which reversibly forms a σ-complex, SHg^{++}. Since the proper thermodynamic indicators have not been found, the function can better be expressed in terms of the rate of mercuration of benzene, in analogy with the expression of h_0 and H_0 in terms of the rates of certain acid-catalyzed reactions.[28,29] Here

$$v = \frac{k_2}{K_m}\,(C_6H_6)\,hg_0\frac{f_{C_6H_6HgH^{++}}}{f_{\pm}} = k_{obsd}(C_6H_6)(Hg^{++})$$

where $K_m = a_{C_6H_6}a_{Hg^{++}}/a_{C_6H_5HgH^{++}}$, and $f_{\pm}$ is the activity coefficient of the transition state. A simplification may be obtained by noting that, in dilute solution, hg_0 approaches (Hg^{++}), so that k_{obsd} approaches $k_2/K_m = k^0_{obsd}$. We further assume the same type of regularities for the activity coefficient ratios as those which are postulated for the H_0 function. The operational equation for Hg_0 (i.e., for $-\log hg_0$) is then

$$-Hg_0 - \log (Hg^{++}) = \log k_{obsd}/k^0_{obsd}$$

The values of $-Hg_0 - \log (Hg^{++})$ which are listed in Table III have been calculated from this equation and from the value of 1.70×10^{-3} l./mole min. for k^0_{obsd} with 0.2 M mercuric perchlorate. The curve for the logarithm of the second-order rate constant against the negative logarithm of the activity of water (Fig. 5) parallels Hg_0; thus the logarithm of k_{obsd} for the mercuration of any aromatic compound is predicted as a constant characteristic of the specific substrate, plus a common function of the activity of water.

However, since the transition state for mercuration explicitly includes a molecule of water (see section on reaction mechanism), the operational equation for Hg_0 given above does not truly correspond to the thermodynamic or kinetic definitions, but differs from these by log a_w. But Bunnett[20] has shown that many reactions which approximately follow H_0 also involve one (or more) molecules of water in their transition states, so that a strict application of the Hammett–Zucker hypothesis, or its analog for mercuration, is not warranted. Probably Hg_0 will prove neither more nor less clearly defined than H_0, when the latter is determined by kinetic methods. Although our formulation cannot offer more than a crude approximation, we predict that the Hg_0 function will roughly correlate rates of mercuration.

The Reaction Mechanism.—The primary deuterium isotope effect for mercuration in aqueous solution is large (Table V), as it is in acetic acid solution.[38,39] Therefore, mercuration follows a two-step pathway, with rate-limiting deprotonation.

$$Hg^{++} + C_6H_6 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C_6H_5HgH^{++}$$

$$C_6H_5HgH^{++} + H_2O \xrightarrow{k_2} C_6H_5Hg^+ + H_3O^+$$

where $v = k_{obsd}(C_6H_6)(Hg^{++})$, and $k_{obsd} = k_1k_2/(k_{-1} + k_2)$.

If it is assumed that k_1 and k_{-1} are practically unaffected by isotopic substitution in the benzene, and further that k_{2H}/k_{2D} is 7.0, then the data of Table V lead to ratios of k_{2H}/k_1 ranging from 0.04 in dilute solution to 0.6 in 6.65 M perchloric acid. Thus the major effect upon the rate must be a large increase in k_1 as solutions of higher ionic content are employed. The increase in k_1 is caused by the increase in the activity coefficients of the ionic reagents in concentrated solutions of acids and salts. This reversal[40] of the Debye–Hückel limiting law amounts to the salting out of ions, where there is insufficient water for solvation or for the separation of ions of like charge.

The observed decrease in k_H/k_D upon decreasing the activity of water in the system may be understood in terms of the effect of water on k_2 and k_{-1}. The removal of a Hg^{++} requires more water than the removal of a proton from the intermediate $C_6H_5HgH^{++}$; as the activity of water is decreased, k_2 becomes larger relative to k_{-1}.

The σ^+-Value for the Mercury(II) Substituent.— Presumably the modified[41] Hammett equation, log $k/k^0 = \rho\sigma^+$, is applicable to mercuration. Schramm[16] found that in aqueous solution benzene is mercurated 10^3–10^4 times as fast as is nitrobenzene. Using $+0.71$ as the σ^+-value for a m-nitro group, an estimate of about -5 can be obtained for the ρ-constant for mercuration in aqueous solution; this agrees with the value in acetic acid as solvent.[41]

Table VI give the values of α, the ratio of the rate constant for the mercuration of phenylmercuric ion to that for the mercuration of benzene. From these data and a value of -5 for ρ, the value of σ^+ for the mercury-(II) substituent (averaged over o, m, and p) can be calculated; it varies, depending on the solution used for mercuration, from 0.09 to 0.16.

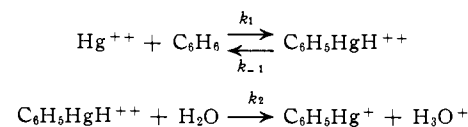(34) K. N. Bascombe and R. P. Bell, *Discussions Faraday Soc.*, **24**, 158 (1957).

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(40) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 3rd Ed., Reinhold Publishing Corp., New York, N. Y., 1958, Fig. 13-4-1, p. 561.

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<div align="center">CHART I</div>

$$\dot{M} = -kM(B + \alpha P_1 + \beta P_2) \qquad \frac{dm}{dt} = -\frac{m}{r}(1 + \alpha p_1 + \beta p_2) \qquad \frac{dm}{dy} = -\frac{1}{r}(1 + \alpha p_1 + \beta p_2) \quad (1)$$

$$\dot{P_1} = kM(B - \alpha P_1) \qquad dp_1/dt = m(1 - \alpha p_1) \qquad dp_1/dy = 1 - \alpha p_1 \quad (2)$$

$$\dot{P_2} = kM(\alpha P_1 - \beta P_2) \qquad dp_2/dt = m(\alpha p_1 - \beta p_2) \qquad dp_2/dy = \alpha p_1 - \beta p_2 \quad (3)$$

$$\dot{P_3} = kM\beta P_2 \qquad dp_3/dt = \beta m p_2 \qquad dp_3/dy = \beta p_2 \quad (4)$$

These are surprisingly small values, since a positively charged substituent would be expected to act as a powerful deactivator. (In contrast, the σ-value for a m-trimethylammonium group[42] is 1.02.) The low value of σ^+ is not caused by effective conversion of the phenylmercuric ion to phenylmercuric hydroxide; the ionization constant[43] of that base is 1×10^{-10}. Nor is mesomeric interaction with the ring likely for a fourth-row element like mercury; further (contrary to experiment) such interaction would favor o- and p-substitution. Presumably only weak deactivation is observed for the mercury(II) substituent because the charge is not concentrated, as it is in the trimethylammonium salt group. The mercury atom is solvated by direct coordination to water molecules, and the positive charge can be distributed among several protons remote from the reaction center, in a region of higher local dielectric constant. Thus the effect of the positive charge is greatly diminished.

The values of both α and β decrease with decreasing water activity. The mercuration reaction then becomes more selective as regards polymercuration as the reaction proceeds more rapidly. This paradox may be resolved by consideration of the physical chemistry of concentrated solutions. In highly ionic solutions, less water is available to solvate the mercuric ions. This leaves more positive charge remaining on the mercury, which thus becomes more nearly like a tri-methylammonium substituent, that is, more deactivating. The rate of polymercuration, relative to that of monomercuration, therefore diminishes in the more concentrated solutions.

Mathematical Appendix
Differential Equations, Solved for Infinite Time.—
Let M = molar concentration of mercuric ion, with an initial value of M_0, let B = molar concentration of benzene (independent of time), and let P_1, P_2, and P_3 = the molar concentrations of mono-, di-, and trimer-curated species, with values of zero at zero time. Let k, αk, and βk be the second-order rate constants for the reaction of mercuric ion with benzene, phenylmercuric ion, and phenylene-bis-mercuric ion, respectively (see chemical equations in Introduction). Then the differential equations are those in the left-hand column of Chart I. These equations may be transformed into an equivalent set with dimensionless variables by the substitutions $m = M/M_0$, $p_1 = P_1/B$, $p_2 = P_2/B$, $p_3 = P_3/B$, $r = M_0/B$, and $t = kM_0 t_r$, where t_r is the reaction time. This set of differential equations appears in the middle column.

Further simplification is achieved by the use of the parameter[44] y, defined by $y = \int_0^t m\, dt$. This transformed set of differential equations appears in the right-hand column above, with the boundary conditions that at $y = 0$, $m = 1$ and $p_1 = p_2 = p_3 = 0$.

Equation 2 is separable; integration leads to the relationship

$$\alpha p_1 = 1 - e^{-\alpha y} \qquad (5)$$

(42) J. D. Roberts, R. A. Clement, and J. J. Drysdale, *J. Am. Chem. Soc.*, **73**, 2181 (1951).

(43) T. D. Waugh, H. F. Walton, and J. A. Laswick, *J. Phys. Chem.*, **59**, 395 (1955); S. S. Parikh and T. R. Sweet, *ibid.*, **65**, 1909 (1961).

(44) D. French, *J. Am. Chem. Soc.*, **72**, 4806 (1950).

Substitution of eq. 5 into eq. 3 leads to a standard linear differential equation, which on integration yields

$$p_2 = \frac{1}{\beta(\beta - \alpha)}\{\beta(1 - e^{-\alpha y}) - \alpha(1 - e^{-\beta y})\} \qquad (6)$$

Substitution for p_2 from eq. 6 into eq. 4 gives an equation which can be integrated directly to yield

$$p_3 = y - \frac{1}{\alpha} - \frac{1}{\beta} + \frac{1}{\beta - \alpha}\left(\frac{\beta}{\alpha} e^{-\alpha y} - \frac{\alpha}{\beta} e^{-\beta y}\right) \qquad (7)$$

Substitution of eq. 7 into eq. 1 and integration gives

$$r(1 - m) = 3y - \frac{2}{\alpha} - \frac{1}{\beta} + \frac{1}{\beta - \alpha}\left(\frac{2\beta}{\alpha} e^{-\alpha y} - e^{-\alpha y} - \frac{\alpha}{\beta} e^{-\beta y}\right) \qquad (8)$$

In principle, eq. 8 could be further integrated, since $m = dy/dt$. However, the resulting integral cannot be expressed in terms of ordinary functions. Fortunately, the complete solution is not required, but only the behavior in the limit as t becomes very large. Assuming complete consumption of mercuric ion at infinite time, eq. 8 becomes

$$3y + \frac{1}{\alpha - \beta}\left(\frac{\alpha}{\beta} e^{-\beta y} + e^{-\alpha y} - \frac{2\beta}{\alpha} e^{-\alpha y}\right) - r - \frac{2}{\alpha} - \frac{1}{\beta} = 0 \qquad (9)$$

Equations 5, 7, and 9 can be combined to yield the relationship, for infinite time

$$y = \frac{1}{2}(r + p_1 - p_3) = p_1 + p_2 + p_3 \qquad (10)$$

Substitution of eq. 10 into eq. 5 leaves a transcendental equation in α, which can be solved numerically. Values of α and y can be substituted into eq. 7, which can then be solved for β.

In order to carry out these numerical solutions, values of p_1, p_2, and p_3 are required. The v.p.c. analysis determines only the ratio of these quantities. However, the individual values may be obtained by combining the v.p.c. data with the stoichiometric relationship that, at infinite time, $r = p_1 + 2p_2 + 3p_3$. The results of the computations are presented in Table VI.

Analog Simulation of the Differential Equations.—
Each concentration was scaled to a maximum value of unity by the following transformation to dimensionless variables: $m = M/M_0$, $q_1 = P_1/M_0$, $q_2 = 2P_2/M_0$, $q_3 = 3P_3/M_0$, and $\tau = k_{obsd}t_r$. The differential equations then become

$$dm/d\tau = m + \alpha rmq_1 + {}^1/_2\beta rmq_2$$
$$dq_1/d\tau = m - \alpha rmq_1$$
$$dq_2/d\tau = 2\alpha rmq_1 - \beta rmq_2$$
$$dq_3/d\tau = {}^3/_2\beta rmq_2$$

with the initial conditions that at $\tau = 0$, $m = 1$, and $q_1 = q_2 = q_3 = 0$.

In the PACE electronic analog computer, 100 v. is the maximum capacity of the amplifier output, so the maximum value (unity) of the dimensionless variables was set equal to 100 v. The computer integrates with respect to time in seconds, so that the natural "half-time" is 0.7 sec. For convenience, and to allow the servomultiplier to follow the quantity m mechanically, the time scale of the machine was slowed by a factor of ten, by decreasing the input to each integrator by a factor of ten.

The experimentally observed quantity is the fraction of mercuration, represented by the quantity $1 - m$,

which drives the y-axis of the Variplotter. For most experiments (where the reactions were carried only to 50% completion), the sensitivity for the pen was set at 5 v./in., so that 50% completion would produce full scale deflection.

Figure 6 shows the circuit diagram. The mechanical arm of the multiplier was driven by $m/100$, which taps off the fraction m of both q_1 and q_2, and so generates the products mq_1 and mq_2. The outputs labeled Hg, Mono, Di, and Tri produce m, $-q_1$, $-q_2$, and $-q_3$, respectively.

Attenuators 1 to 8 were set with the indicated coefficients, using the experimental values of α, β, and r. The circuit is provided with three extra amplifiers which generate the quantity $1 - m - q_1 - q_2 - q_3$ at the output marked Z. Stoichiometry requires that this quantity be zero, so that digital readout of Z provided a check on the correctness of the analog program. A further check on internal consistency was provided by allowing the machine simulation to run until m had decreased to 0.1 v., corresponding to 99.9% of reaction. Digital readout of q_1, q_2, and q_3 allowed the computation of α and β; these values were found to correspond within 1% to those originally introduced into the program. It would have been possible to determine α and β by adjusting the appropriate attenuators until the ratios of products, determined by v.p.c., could be reproduced. However, the analytic method is preferred, as more direct; the analog method would require the successive adjustment of six potentiometers, and might be subject to electronic error.

Time Generation in Analog Simulation.—Integrating a constant voltage generates time to drive the x-axis of the Variplotter. The voltage was chosen as 100 κ volts. The value of κ was then found by adjusting the attenuator (number 9 on the diagram) until the experimental data (in dimensionless variables) were reproduced by the computer. Only this one variable was adjusted; the rather complex shapes were thus fitted with a single rate constant. The relationship between the first-order rate constant and κ may be understood by considering the case where $\alpha = \beta = 0$. Let Θ be the machine time, in seconds, and let the
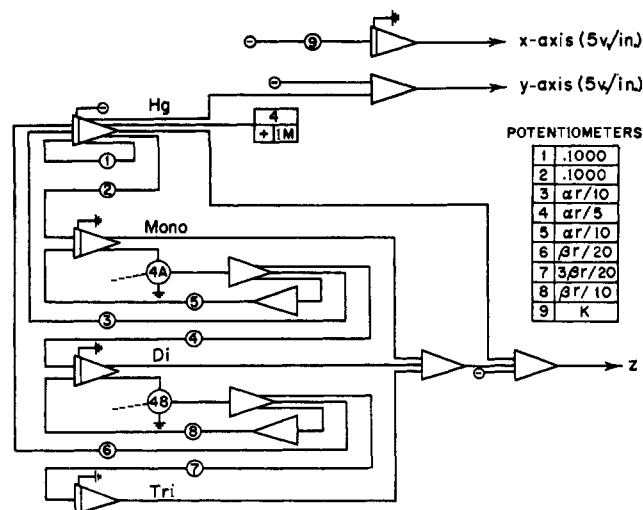

Fig. 6.—The circuit diagram for the PACE analog computer. Open triangles are summing amplifiers, barred triangles are integrators, the rectangle represents the servomultiplier, and open circles are attenuators. The numbers within the symbols are for identification purposes only.

horizontal scale on the graph paper be n min. (reaction time)/inch. Assume that the potentiometer has been adjusted so that the machine traces a curve through the experimental points. After Θ seconds, the recorder arm has traveled

$$(100\kappa \text{ v.}) (\Theta \text{ sec.})/(5 \text{ v. per in.}) = 20 \kappa\Theta \text{ in.}$$

On the y-axis, the pen plots $(1 - e^{-\Theta/10})$, the solution to the simplified differential equation, with the motion reduced by a factor of $1/10$ due to the retardation factor deliberately introduced on each integrating amplifier. The equation with $\alpha = \beta = 0$ would be $(1 - e^{-kt_r})$ vs. t_r. Therefore we may identify $\Theta/10$ with kt_r. But t_r must be t_r/n inches along the horizontal axis, or $x = t_r/n$. From the above, we also have $x = 20\kappa\Theta$, and we may solve to obtain $k = 0.005/n\kappa$.
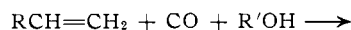

Carboxyalkylation Reactions Catalyzed by Cobalt Carbonylate Ion

BY R. F. HECK AND D. S. BRESLOW

Acylcobalt carbonyls react with alcohols to produce esters and cobalt hydrocarbonyl. The reaction is more rapid in the presence of sodium alkoxides, sodium cobalt carbonylate being produced in addition to the ester. A catalytic carboxylation of alkyl halides, sulfates, or sulfonates has been demonstrated using cobalt carbonylate ion as catalyst in the presence of a base, an alcohol (or water), and carbon monoxide. If unhindered amines are used as the base, amides are obtained. This reaction takes place under mild conditions with reactive halides, and yields are reasonable. If the reaction is carried out at 50° or below, isomerization is not observed and only the expected carboxylated derivatives are found. Thus, the reaction should be of preparative value.

Introduction

The carboxylation of olefins with carbon monoxide in the presence of water or alcohols, catalyzed by nickel or cobalt carbonyls, has been known for several years.[1] Mixtures of isomeric acids or esters are produced. More

$$RCH=CH_2 + CO + R'OH \longrightarrow$$
$$RCH_2CH_2COOR' + \overset{\displaystyle COOR'}{\underset{\displaystyle RCHCH_3}{|}}$$

recently, Chiusoli has reported a carboxylation of allylic halides with carbon monoxide and water or alcohols under unusually mild conditions using a nickel carbonyl catalyst. The products are mixtures of 2- and 3-butenoic acids or esters.[2]

$$CH_2=CHCH_2X + CO + ROH \xrightarrow{Ni(CO)_4}$$
$$CH_2=CHCH_2COOR + CH_3CH=CHCOOR + HX$$
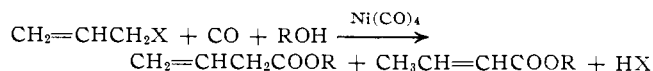
The close similarity between the hydroformylation and carboxylation reactions with a cobalt catalyst, differing only in the use of hydrogen in the former and

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(2) G. P. Chiusoli, *ibid.*, **41**, 503 (1959); *Gazz. chim. ital.*, **89**, 1332 (1959).