described for uranium(IV) borohydride.[2] The data for the monomethyl compound are recorded in Table I.

TABLE I

VAPOR PRESSURES OF THE MONOMETHYL DERIVATIVE OF URANIUM(IV) BOROHYDRIDE

The calculated pressures were obtained from the equation:

$$\log P = -3,160/T + 10,690$$

Temp., °C.	25.1	31.4	38.1	45.4	50.7	58.0	65.6
P, mm., obsd.	1.06	2.13	3.37	5.56	8.52	14.6	25.8
P, mm., calcd.	1.24	2.05	3.44	5.87	8.53	14.0	23.4

In Table II the data for the tetramethyl derivative are recorded.

TABLE II

VAPOR PRESSURES OF THE TETRAMETHYL DERIVATIVE OF URANIUM(IV) BOROHYDRIDE

The calculated pressures were obtained from the equation:

$$\log P = -2,960/T + 8.815$$

Temp., °C.	40.1	45.6	53.2	60.3	65.3	70.6	73.7
P, mm., obsd.	0.24	0.34	0.51	0.84	1.03	1.66	1.93
P, mm., calcd.	0.23	0.34	0.55	0.86	1.17	1.60	1.91

Triethylboron and Uranium Borohydride.—Uranium borohydride, 9.6 mmoles, and 5.0 mmoles of triethylboron were heated in an evacuated reaction tube at 60° for two hours. The contents of the tube were then distilled through a series of U-tubes at −20, −80 and −196°. The −20° tube showed a tinge of green within a few minutes and within 20 min. there was green color in the −80° tube. Since very little material distilled from the reaction vessel at room temperature, the latter was heated to 70°. A ring of colorless, oily liquid was noted in the reaction vessel, just above the heating bath. The liquid might have been a compound analogous to the tetramethyl derivative but insufficient material was obtained to attempt its purification and identification.

The material collected at −20° was distilled through a second series of U-tubes at 0, −20 and −80° for 18 hours. About 100 mg. passed through the −20° trap into the −80° tube. The condensate in the latter was, however, obviously still a mixture of green and of lighter colored material. Neither the bulk of the material, trapped at 0°, nor that collected at −20° was very volatile and could not be handled effectively in the vacuum equipment. The difficulty of purification was enhanced by the fact that the volatility of the ethyldiboranes, formed in the reaction, does not differ greatly from that of the uranium compounds.

Analyses (which need not be reported in detail) of the various fractions obtained, showed that the uranium-to-boron ratio in all fractions was approximately 1:4, but the carbon content did not correspond to any of the possible ethyluranium borohydrides.

Uranium borohydride was also treated with triisopropylboron and tri-*t*-butylboron. However, the results were similar—no pure compound could be isolated from the complex reaction mixtures.

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CHICAGO, ILL.

NOTES

A Suggested Reaction Mechanism for the Copolymerization of Ethylene and Carbon Monoxide

BY W. G. BARB

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Brubaker, Coffmann and Hoehn[1] have recently discovered that polyketones can be prepared by copolymerizing carbon monoxide and ethylene in cyclohexane solution, using di-(*t*-butyl) peroxide as catalyst. Their paper gives, amongst other data, information about the effect of the monomer ratio and of the total pressure on the composition of the resulting copolymer and the yield obtained in a given time.

There is an obvious formal similarity between this reaction and the formation of polysulfones from olefins and sulfur dioxide. The kinetics of the latter have recently been investigated[2,3] and it has been shown that sulfur dioxide units are incorporatedin to the polymer chain by reaction of a 1:1 complex of sulfur dioxide and the olefin; this contrasts with copolymerizations of two vinyl compounds, where it is generally accepted that the original monomeric units react (see, *e.g.*, review by Mayo and Walling[4]). It is therefore of interest to examine whether the similarity between polysulfone and polyketone formation extends to the reaction mechanisms. One feature of the data of Brubaker, *et al.*,[1] immediately suggests that the usual copolymer composition equation[4] which holds for vinyl copolymerizations, and which only involves the *ratio* of the monomer concentrations, is not directly applicable in this system; namely, the composition of the copolymer obtained at a given monomer ratio varies greatly with the total pressure, *i.e.*, with the absolute monomer concentration.

It is therefore suggested that the reaction occurs by the usual type of free-radical polymerization processes but that, by analogy with polysulfone formation,[2] the reactants are the olefin M and a 1:1 complex C of the olefin and carbon monoxide; and that the concentration [C] of the complex is given by

$$[\mathrm{C}] = K[\mathrm{M}][\mathrm{CO}]$$

where [M] and [CO] are the total concentrations of olefin and carbon monoxide (*i.e.*, the equilibrium constant K is assumed to be small).

From the four possible propagation reactions (R = remainder of polymer radical), *viz.*

$$\begin{array}{ll} \mathrm{R{-}C\cdot} + \mathrm{C} \longrightarrow \mathrm{R{-}C\cdot} & k_{\mathrm{CC}} \\ \mathrm{R{-}C\cdot} + \mathrm{M} \longrightarrow \mathrm{R{-}M\cdot} & k_{\mathrm{CM}} \\ \mathrm{R{-}M\cdot} + \mathrm{C} \longrightarrow \mathrm{R{-}C\cdot} & k_{\mathrm{MC}} \\ \mathrm{R{-}M\cdot} + \mathrm{M} \longrightarrow \mathrm{R{-}M\cdot} & k_{\mathrm{MM}} \end{array}$$

[1] M. M. Brubaker, D. D. Coffmann and H. H. Hoehn, THIS JOURNAL, **74**, 1509 (1952).

[2] W. G. Barb, *Proc. Roy. Soc.* (*London*), **A212**, 66, 177 (1952).

[3] F. S. Dainton and K. J. Ivin, *ibid.*, **A212**, 96, 207 (1952).

[4] F. R. Mayo and C. Walling, *Chem. Revs.*, **46**, 191 (1950).

we obtain, applying the copolymer composition equation,

$$\rho = \frac{\text{rate of reaction of olefin}}{\text{rate of reaction of complex}} = \frac{[\mathrm{M}]}{[\mathrm{C}]}\,\frac{r_{\mathrm{M}}[\mathrm{M}] + [\mathrm{C}]}{r_{\mathrm{C}}[\mathrm{C}] + [\mathrm{M}]} \qquad (1)$$

where r = reactivity ratio, *i.e.*, $r_{\mathrm{M}} = k_{\mathrm{MM}}/k_{\mathrm{MC}}$ and $r_{\mathrm{C}} = k_{\mathrm{CC}}/k_{\mathrm{CM}}$.

If we assume further that the complex C reacts so as to give a terminal M· group rather than a terminal CO·, and that the penultimate unit of the radical does not affect the reactivity ratio, then

$$k_{\mathrm{CC}}/k_{\mathrm{CM}} = k_{\mathrm{MC}}/k_{\mathrm{MM}},\ \textit{i.e.},\ r_{\mathrm{C}} = 1/r_{\mathrm{M}}$$

Equation (1) thus becomes, very simply

$$\rho = r_{\mathrm{M}}[\mathrm{M}]/[\mathrm{C}] \qquad (2)$$

and

$$n = \text{ratio of M to CO in copolymer} = 1 + \rho = 1 + r_{\mathrm{M}}[\mathrm{M}]/[\mathrm{C}] = 1 + r_{\mathrm{M}}/K[\mathrm{CO}] \qquad (3)$$

i.e., n is now a function of the absolute carbon monoxide concentration. (We note that equation (2) corresponds to an "ideal" copolymerization as defined by Wall,[5] since the relative reactivity of the two reacting monomers (C and M) is the same toward all radicals in the system.)

To analyze the data of Brubaker, *et al.*,[1] in terms of equation (3) the monomer concentrations in solution must be related to pressures in the gas phase. This was done as follows.

(a).—The Ostwald absorption coefficients α_{CO} and $\alpha_{\mathrm{C_2H_4}}$ were assumed constant up to partial pressures of about 200 atmospheres (a single experiment reported for a higher pressure was omitted from this analysis). This assumption regarding α seems to hold to within about 20% for a similar range of pressures in the case of several gases above their critical temperature, *e.g.*, CH_4 and N_2 in various organic solvents. (See data listed by Seidell.[6,7]) The mean values of [CO] and [C_2H_4] can therefore be taken proportional to $\bar{p}_{\mathrm{CO}}/D$ and $\bar{p}_{\mathrm{C_2H_4}}/D$, respectively, where $\bar{p}$ = mean partial pressure during the experiment and D = volume of solution per volume of solvent. Equation (3) thus becomes

$$(n - 1) \propto D/\bar{p}_{\mathrm{CO}} \qquad (4)$$

(b).—$\bar{p}_{\mathrm{CO}}$ and $\bar{p}_{\mathrm{C_2H_4}}$ were calculated from the feed composition, the yield and composition of the polymer and the volume of the solution and the gas phase, assuming values of α as in (c) and ideality of the gas phase. The maximum difference between $\bar{p}_{\mathrm{CO}}$ and the corresponding inital value p_{CO} was 35%, and that between $\bar{p}_{\mathrm{C_2H_4}}$ and $p_{\mathrm{C_2H_4}}$ rather less.

(c).—To calculate D, the actual values of α were assumed to be: $\alpha_{\mathrm{CO}} = 0.3$, $\alpha_{\mathrm{C_2H_4}} = 1.0$, for cyclohexane at 135°. (These figures are suggested by data for other organic solvents at various temperatures[6,7]; for both gases, α is very similar in different organic liquids.) Hence the weights W_{CO} and $W_{\mathrm{C_2H_4}}$, in grams dissolved per ml. of cyclohexane, were calculated and inserted in the relation

$$D = W_{\mathrm{CO}}/0.5 + W_{\mathrm{C_2H_4}}/0.3$$

The "densities" 0.5 and 0.3 are extrapolated from data below the critical temperature, by assuming a decrease in density of 0.1 per 100°. In this calculation no allowance is made for the considerable dilution by the reaction product. However it is clear that if the solubilities of CO and C_2H_4 in the polyketone are similar to those in cyclohexane the effect on the copolymer composition should be slight.

The calculation of D and $\bar{p}_{\mathrm{CO}}$ is not very sensitive to the numerical values chosen for the various constants. Thus (i) D never differs greatly from unity, the maximum value for any experiment included in the present analysis being 1.55, and (ii) $\bar{p}$ is little affected by the exact values of α since the greater part of both monomers is present in the gas phase.

Figure 1 shows the data of Brubaker, *et al.*,[1] relating to the dependence of n on the monomer concentration ratio and on the total pressure at a given feed composition. There is reasonable accord with equation (4); however, this cannot be regarded as more than supporting the plausibility of the suggested mechanism. At the same time, if CO were assumed to react in its molecular form, the variation of n with total pressure could only arise from (a) somewhat different *mean* compositions of the reaction mixture due to different conversions or (b) an effect of pressure on the solubility ratio of CO to C_2H_4. Of these, (a) can be shown to produce a converse trend in n to that observed, and would also require all polymers prepared at the same feed to have compositions to the same side of the feed composition, which is not the case (Table I, ref. (1)); (b) on the other hand would require the unjustifiable assumption that the solubility *ratio* was approximately proportional to the total pressure.

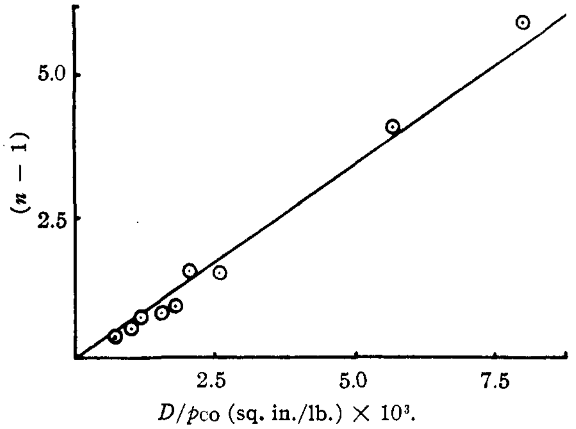

Fig. 1.

An analysis of reaction rate data is not possible without additional information, *e.g.*, on the dependence of the rate of initiation I on monomer concentration. However it is clear that since the usual copolymer composition equation does not explain the stoichiometry data if C_2H_4 and CO are taken to be the reacting entities, such a reaction scheme also cannot account simultaneously for $-d[\mathrm{CO}]/dt$ and $-d[\mathrm{C_2H_4}]/dt$. It may be noted that the mechanism proposed in this Note leads to very simple rate expressions since all radicals in the

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[5] F. T. Wall, THIS JOURNAL, 66, 2050 (1944).

[6] A. Seidell, "Solubilities of Inorganic and Metal Organic Compounds," 3rd Ed., D. Van Nostrand Co., Inc., New York, N. Y., 1940.

[7] A. Seidell, "Solubilities of Organic Compounds," 3rd Ed., D. Van Nostrand Co., Inc., New York, N. Y., 1941.

system are similar and there is only one termination reaction; *e.g.*, it is found that

$$-d[CO]/dt \propto I^{1/2}[CO][M] \qquad (5)$$

It should be added that the inhomogeneity of the polyketone product[1] is not necessarily due to a multiplicity of mechanisms, but very probably arises from (i) the change in p_{CO} and $p_{C_2H_4}$ during reaction, if the polymer composition is not the same as the feed composition, and (ii) the increase in molecular weight caused by a decrease in catalyst concentration during the reaction.

Since this Note was originally submitted, some further data and a proposed interpretation assuming CO and C_2H_4 to be reacting entities have been published by Coffman, *et al.*[8] Of these new data, the temperature-dependence which the authors report would follow either from their mechanism or that suggested here. Again, the expected composition of the azeotropic mixture under conditions where Coffman, *et al.*, calculate 46% would be very similar, *viz.*, 44.5%, on the scheme in this Note; the mean experimental value, 45.2%, does not decide between these alternatives. On the other hand, the writer's assumption of a CO/C_2H_4 complex does seem to have the advantage of explaining, at least qualitatively, the reported dependence of the azeotropic composition on the total pressure[8]; this would merely be a special case of the variation of polymer composition with total pressure, discussed above in connection with the data of Brubaker, *et al.*[1] Finally, it is to be pointed out that much of the work of Coffman, *et al.*, has been carried out under heterogeneous conditions, in the absence of a solvent, and that this may constitute a kinetically more complicated system than obtains in solution.

I should like to thank Dr. C. H. Bamford for a discussion of this paper.

[8] D. D. Coffman, P. S. Pinkney, F. T. Wall, W. H. Wood and H. S. Young, THIS JOURNAL, **74**, 3391 (1952).

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The Carbethoxylation Products of *p*-Aminoacetophenone and *p*-Dimethylaminoacetophenone[1]

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During the course of a program of synthesis of β-keto esters, the method of carbethoxylating the α-carbon atom of ketones by replacement of active hydrogen using sodium amide and ethyl carbonate[2] was applied to *p*-aminoacetophenone (I) in the hope that the α-carbon might be carbethoxylated as well as the nitrogen atom. In spite of the use of very large excesses of reactants and elevated temperatures, however, the only obtainable product was ethyl *p*-acetylphenylurethan (II) resulting from attack on the nitrogen alone, nor was it possible to effect further carbethoxylation of II by the same procedure subsequent to its isolation.

The structure of II was established by elementary analysis, cryoscopic molecular weight determination, alkaline hydrolysis to I, comparison with an authentic sample obtained from I and ethyl chlorocarbonate,[3] and nitration to ethyl 2-nitro-4-acetylphenylurethan[3] previously synthesized. It was further characterized by the preparation of its 2,4-dinitrophenylhydrazone, hitherto unknown.

p-Dimethylaminoacetophenone (III) was successfully carbethoxylated by the same procedure to yield the new ethyl *p*-dimethylaminobenzoylacetate (IV) in low yields. The structure of IV was established by elementary analysis, molecular weight determination, hydrolysis to III and by conversion to 1-(2,4-dinitrophenyl)-3-(*p*-dimethylaminophenyl)-5-pyrazolone and 3-(*p*-dimethylaminophenyl)-5-isoxazolone, both new compounds.

It is interesting to note that both II and IV are very resistant to acid hydrolysis, but they are easily cleaved by 5% alcoholic potassium hydroxide.

Experimental

Ethyl *p*-Acetylphenylurethan (II).—Four hundred ml. of liquid ammonia was placed in a 1-l. three-neck flask fitted with a reflux condenser and Hershberg stirrer followed by 1 g. of anhydrous ferric chloride and 13.8 g. (0.6 atom) of clean sodium. As soon as the reaction forming sodamide was complete, a slurry of 27 g. (0.2 mole) of I in 600 ml. dry ether was added all at once. During two hours stirring, the evaporating ammonia was replaced by an equal volume of dry ether. Then 71 g. (0.6 mole) of diethyl carbonate was added and the whole suspension was refluxed for two hours with vigorous stirring. Finally the reaction mixture was slowly poured with stirring into 50 ml. of acetic acid and 500 g. of ice. The product was filtered dry and recrystallized from ethanol yielding 28 g. (68%) of pale yellow crystals melting at 157–158°. Even when the molar ratio of sodamide and ethyl carbonate to II was raised to six, no other product was obtained—only slight increase in yield.

II is insoluble in hot and cold water and ligroin, sparingly soluble in cold benzene and alcohol, quite soluble in acetone, dioxane, hot alcohol and hot benzene. It is soluble in concentrated sulfuric acid producing an orange-red color, but it is recovered unchanged upon dilution.

Anal. Calcd. for $C_{11}H_{13}O_3N$: N, 6.76; mol. wt., 207.2. Found: N, 6.97, 6.82; mol. wt. (Rast method), 206, 202, 201; (cryoscopic, in dioxane solution), 207.3, 205.8, 208.1.

Ethyl-*p*-acetylphenylurethan-2,4-dinitrophenylhydrazone was prepared in the usual manner. It occurs as orange-red crystals melting at 232–234°.

Anal. Calcd. for $C_{17}H_{17}O_6N$: N, 18.08. Found: N, 18.30, 18.19.

Ethyl *p*-Dimethylaminobenzoylacetate (IV).—A suspension of 0.26 mole of sodamide in 300 ml. of liquid ammonia was prepared in the same manner described above. After the ammonia had evaporated while being simultaneously replaced with dry ether, 16 g. (0.1 mole) of *p*-dimethylaminoacetophenone[4] dissolved in 300 ml. of ether was added. The mixture was then refluxed two hours. Finally 30 g. (0.254 mole) of diethyl carbonate was added, and stirring and refluxing were continued for four hours. After cooling, 500 ml. of water was cautiously added. The ether phase was washed, dried with anhydrous sodium sulfate and evaporated to dryness. After recrystallization from ethanol–water 2.5 g. (11%) of pale yellow needles melting at 64° was obtained.

IV is very slightly soluble in cold water and ligroin. It is quite soluble in 5% aqueous hydrochloric acid, warm 5% aqueous sodium hydroxide, ether, dioxane, acetone, hot alcohol and hot benzene.

Anal. Calcd. for $C_{13}H_{17}O_3N$: N, 5.95; mol. wt., 235.3. Found: N, 6.08, 6.17; mol. wt. (cryoscopic, in dioxane), 234.0, 233.6.

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[1] Abstracted from a thesis presented by Chao-Yuan Chu in partial fulfillment of the requirements for a degree of Master of Science at Brigham Young University.

[2] R. Levine and C. R. Hauser, THIS JOURNAL, **66**, 1768 (1944).

[3] Chr. W. Raadsveld, *Rec. trav. chim.*, **54**, 813 (1935).

[4] Prepared by treatment of *p*-aminoacetophenone with dimethyl sulfate: Weil, *Monatsh.*, **29**, 905 (1908).