of this amine alane from the elements in contrast to the difficulty of preparing monofunctional amine alanes is attributed to the heat of polymerization (or crystallization) of the product as well as to the basicity of the amine.

Preliminary studies show that other tertiary diamines, such as tetramethylethylenediamine, as well as secondary and primary amines react with aluminum and hydrogen to form active N–Al–H compounds.

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Oxidation of Vanadium(IV) by Chromium(VI) in Acidic Solution[1]

Sir:

This communication describes results of a kinetic study on the reaction of vanadium(IV) with chromium(VI) in acidic perchlorate solution, the stoichiometry and rate of which had not been described previously.

The reaction was studied spectrophotometrically at a single wave length, 3500 Å. Vanadium(IV) is essentially transparent at this wave length, and vanadium(V) has a molar absorbancy index of 140.6 l. mole^{-1} cm.$^{-1}$. At the single acidity used in these studies, 0.00500 F HClO$_4$, the absorbancy index of chromium(VI) is 1554 l. mole^{-1} cm.$^{-1}$, a maximum. Both vanadium(V) and chromium(VI) obey Beer's law over at least 10-fold concentration ranges. There is no spectral evidence for any association of vanadium(V) and chromium(VI). The relatively rapid reaction of vanadium(IV) and chromium(VI) does not allow determination of whether any complex formation between these species occurs; it has been assumed here that vanadium(IV) interacts negligibly with chromium(VI). Under the present conditions of concentrations and temperature these species dominate: chromium(VI),[2] hydrogen chromate ion HCrO$_4^-$; vanadium(IV),[3] vanadyl ion VO^{2+}; and vanadium(V),[4] pervanadyl ion VO$_2^+$.

The net equation for the reaction of vanadium(IV) and chromium(VI) in this reaction medium is

$$3VO^{2+} + HCrO_4^- + H^+ = 3VO_2^+ + Cr^{3+} + H_2O$$
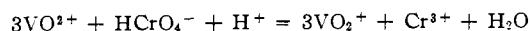
The stoichiometry with regard to oxidation equivalents was established by examination of the equilibrium absorbance at 3500 Å. of solutions with a wide range of compositions. That Cr^{3+}, rather than a hydrolytic polymer, is the chromium(III) product has been assumed and has not yet been verified experimentally.

Preliminary examination of rate data suggested a one-term rate law in which a product, vanadium(V), retards the reaction. Correlation of observed rates and instantaneous concentrations led to this rate law expression at constant acid concentration

$$- d[HCrO_4^-]/dt = k[VO^{2+}]^2[HCrO_4^-]/[VO_2^+] \quad (1)$$

Precise linearity of an integrated form[5] of eq. 1 over a large fraction of reaction together with constancy of

(1) Work performed in the Ames Laboratory of the U. S. Atomic Energy Commission, contribution no. 1467.

(2) J. Y.-P. Tong and E. L. King, *J. Am. Chem. Soc.*, **75**, 6180 (1953).

(3) F. J. C. Rossotti and H. S. Rossotti, *Acta Chem. Scand.*, **9**, 1177 (1955).

(4) F. J. C. Rossotti and H. Rossotti, *ibid.*, **10**, 957 (1956).

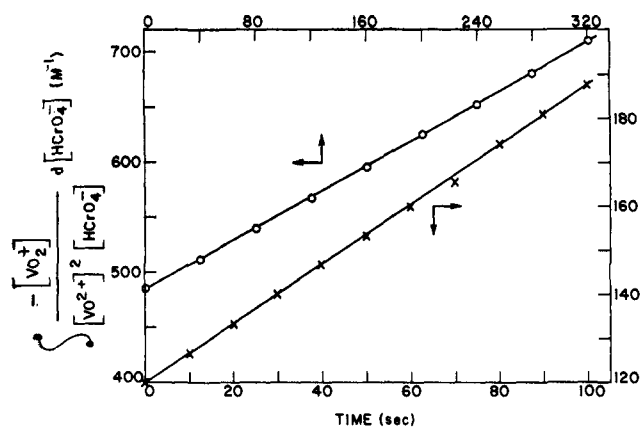(5) This complicated equation is analogous to eq. 9 of ref. 6 and eq. 4 of ref. 7.

Fig. 1.—Linear plots of the integrated form[5] of eq. 1 illustrating conformity to the rate law given. The two runs shown are expt. no. 4 (○) and 5 (×) in Table I.

k from each run establishes that this rate equation holds for all experiments performed, which are listed in Table I. Figure 1 shows such plots for two typical runs. The concentration ranges these data represent amount to variations of ∼6-fold in vanadium(V), ∼20-fold in vanadium(IV), and ∼8-fold in chromium(VI), at constant hydrogen ion concentration.

In the two experiments with added vanadium(V), the vanadium(V) stock solution contributed *ca.* 70% of the final acidity. To eliminate any effect due to this potential error, or due to any slow equilibration among hydrolyzed or polymeric vanadium(V) species, runs in which this same vanadium(V) concentration is generated by prior reaction were carried out. Thus the pairs 3,5 and 4,6 are really the same, except for chromium(III), which is without effect.
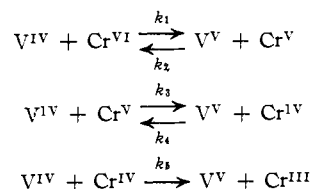
TABLE I
EXPERIMENTALLY DETERMINED VALUES[a] OF THE RATE
CONSTANT k

Expt. no.	Initial concentrations × 10^4(F) [Cr(VI)]	[V(V)]	[V(IV)]	Extent of reaction followed (%)	k (M^{-1} sec.$^{-1}$)
1	1.117		48.85	58–91	0.56
2	1.117		24.42	28–91	0.53
7	1.117		9.77	15–85	0.60
8	1.117		4.885	8–85	0.55
3	1.117	2.988	48.85	27–91	0.66
5	2.113		51.84	14–94	0.66
4	1.117	2.988	24.42	30–90	0.70
6	2.113		27.41	17–90	0.71

Av. 0.62 ± 0.06

[a] 25.00°, 0.00500 F HClO$_4$, $I = 1.00$ F (with LiClO$_4$).

In the reaction of iron(II) and chromium(VI)[6] and in the reaction of chromium(III) and cerium(IV)[7] these are the dominant terms: $k_{Fe}[Fe^{2+}]^2[HCrO_4^-]/[Fe^{3+}]$ and $k_{Ce}[Ce^{IV}]^2[Cr^{3+}]/[Ce^{III}]$, respectively. These rate law forms are the exact analogs of the present findings. Thus the apparent mechanism for this three-equivalent change is

$$V^{IV} + Cr^{VI} \underset{k_2}{\overset{k_1}{\rightleftarrows}} V^V + Cr^V$$

$$V^{IV} + Cr^V \underset{k_4}{\overset{k_3}{\rightleftarrows}} V^V + Cr^{IV}$$

$$V^{IV} + Cr^{IV} \overset{k_5}{\longrightarrow} V^V + Cr^{III}$$

(6) J. H. Espenson and E. L. King, *J. Am. Chem. Soc.*, **85**, 3328 (1963).

(7) J. Y.-P. Tong and E. L. King, *ibid.*, **82**, 3805 (1960).

in which the second step is rate-determining, and with the observed $k = k_1k_3k_2^{-1}$. The analogous change from chromium(V) to chromium(IV), or its reverse, is also the slow step of the other reactions discussed, as well as the slow step in the chromium(III)–chromium(VI) exchange.[8] The explanation for this behavior based on different coordination numbers (4 and 6, respectively) for the intermediates chromium(V) and chromium(IV) has been presented.[6–8]

Further studies on the vanadium(IV)–chromium(VI) system are in progress in an attempt to push the range over which each reactant and product concentration is varied to the very limit of measurement to establish whether the present rate equation remains valid under all attainable concentrations or whether any of the other possible terms can become important. The effect of acid concentration, which was constant in all these experiments, is also under investigation.

(8) C. Altman and E. L. King, J. Am. Chem. Soc., 83, 2825 (1961).

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An Organometal Complex Containing a Copper–Manganese Bond

Sir:

Recent studies[1,2] in these laboratories have yielded a number of compounds containing Au–M bonds (M = Mn, Fe, Co, and W). With a view to solving the more difficult problem of preparing compounds containing Cu–M and Ag–M linkages,[3] we have synthesized the terdentate arsenic ligand 1 which readily forms complexes with the halides of copper(I), silver(I),

$$CH_2As(CH_3)_2$$
$$CH_3—C—CH_2As(CH_3)_2$$
$$CH_2As(CH_3)_2$$
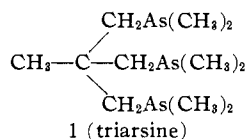
1 (triarsine)

and gold(I). The copper complex, triarsine–CuBr, a monomeric nonelectrolyte evidently containing tetrahedrally coordinated copper(I), reacts with 1 equiv. of sodium pentacarbonylmanganate(−I)[4] in tetrahydrofuran according to the following equation

triarsine–CuBr + Na[Mn(CO)₅] $\longrightarrow$

triarsine–Cu–Mn(CO)₅ + NaBr
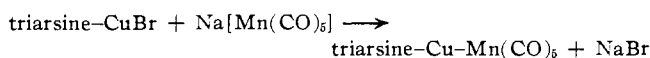
Addition of petroleum ether (b.p. 60–80°) precipitates the yellow-brown product, which can be purified using a dichloromethane–petroleum ether mixture (yield 80%). Anal. Calcd. for $C_{16}H_{27}O_5CuMn$: C, 29.9; H, 4.2; As, 35.0; Cu, 9.9; Mn, 8.5; mol. wt., 642. Found: C, 30.2; H, 4.5; As, 34.7; Cu, 9.7; Mn, 8.2; mol. wt.,[5] 618.

The compound is air-stable and diamagnetic. It is soluble in most common solvents, and in nitrobenzene it is a nonconductor. The infrared spectrum of the

(1) C. E. Coffey, J. Lewis, and R. S. Nyholm, J. Chem. Soc., in press.
(2) A. S. Kasenally, R. S. Nyholm, and M. H. B. Stiddard, ibid., in press.
(3) Professor J. Lewis, et al. (University of Manchester, personal communication), have synthesized recently compounds of the type R–M–Mn(CO)₅, where M = Cu or Ag and R = tertiary phosphine or arsine.
(4) W. Hieber and G. Wagner, Z. Naturforsch., 12b, 478 (1957).
(5) Determined in dichloromethane using a Mechrolab vapor pressure osmometer.

compound in the C–O stretching region has been studied and shows two bands, at 2010 (ms) and 1891 (vs) cm.⁻¹.

Similar experiments starting with the silver(I) complex triarsine–AgBr indicate the formation of an analogous compound containing a Ag–Mn bond, but it is too unstable to be characterized.[6] The triarsine reacts with gold(I) chloride to yield a product triarsine–(–AuCl)₃ in which the arsenic atoms coordinate independently to the gold atoms. This complex, on reaction with sodium pentacarbonylmanganate(−I), gives the expected product triarsine[–Au–Mn(CO)₅]₃.

We are investigating at present the preparation of similar complexes containing Cu–Fe and Cu–Co bonds; these investigations will be described at a later date.

(6) However, by using the aromatic triarsine (o-Me₂As-C₆H₄)₂AsMe we have now synthesized the air-stable complex triarsine–Ag–Mn(CO)₅.

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The Wittig Reaction. I. Synthesis of β,γ-Unsaturated Acids

Sir:

The Wittig reaction has been used to prepare a variety of α,β-unsaturated acids or their esters from carbomethoxymethyltriphenylphosphonium halides.[1–3] In their review on controlling the steric course of the Wittig reaction, Bergel'son and Shemyakin[4] reported the preparation of eleven nonconjugated unsaturated fatty acids. However, no record of the preparation of the unconjugated β,γ-unsaturated acids by the Wittig reaction has come to our attention. Our examination of the literature has not revealed a single reaction or series of reactions which can be designated convenient for the preparation of this type of acid.

We wish to report that the Wittig reaction has been adapted to a versatile synthesis of β,γ-unsaturated acids. Another view of this application of the Wittig reaction is that it permits the lengthening of a carbon chain by three units in one step.

The required intermediate β-carboxyethyltriphenylphosphonium chloride (1) has been prepared according to the method of Denny and Smith.[5] The phosphonium chloride (1) was obtained as a glass which crystallized upon trituration with acetone; 1 was recrystallized by dissolving in chloroform and diluting with acetone to give analytically pure product melting at 196–197°.

Since the preparation of the ylide (3) presumably would go through the intermediate phosphobetaine (2),[5] the reaction has been examined only in dimethyl sulfoxide (DMSO) solution to avoid solubility problems. The usual Wittig procedure of first preparing

(1) G. Fodor and I. Tomoskozi, Tetrahedron Letters, 579 (1961).
(2) S. Trippett and D. M. Walker, Chem. Ind. (London), 990 (1961).
(3) V. F. Kucherov, B. G. Kovalev, I. I. Nazarova, and L. A. Yanovskaya, Izv. Akad. Nauk. SSSR, Otd. Khim. Nauk., 1512 (1960); Chem. Abstr., 55, 1420b (1961).
(4) L. D. Bergel'son and M. M. Shemyakin, Tetrahedron, 19, 149 (1963).
(5) D. B. Denny and L. C. Smith, J. Org. Chem., 27, 3404 (1962).