

on the above theories and the hyperfine splittings arising from C^{13} in natural abundance are in error.

TABLE I
Li⁺TCNQ⁻ SPLITTING CONSTANTS^a

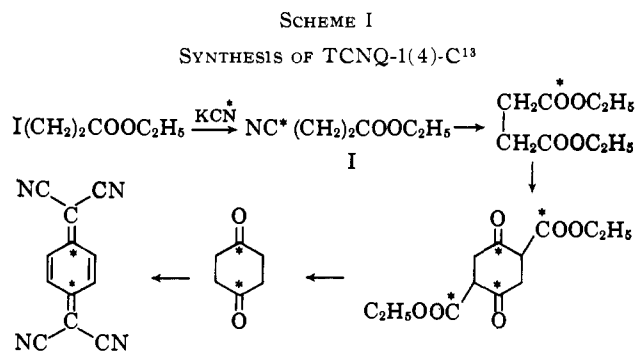
Position ^b or splitting constant	—Calculated, ^c oersted—		—Exptl., oersted—	
	Hückel	McLachlan	Ref. 4	C^{13} substd. ^d
A_{N14}			1.02	1.009 (± 0.005)
A_H			1.44	1.415 (± 0.004)
$C^{13}(1)$	-3.11	-5.02	4.40	1.52 (± 0.04)
$C^{13}(2)$	+0.48	+0.79	0.62	
$C^{13}(7)$	+5.23	+8.49	7.18	
$C^{13}(9)$	-7.17	-8.44	6.38	7.06 (± 0.04)

^a $g = 2.00263 \pm 0.00005$, 10^{-4} M in tetrahydrofuran. ^b See TCNQ structure for position numbering. ^c See ref. 3 and 4. ^d g value and hyperfine splittings obtained by comparison in a dual cavity with a 10^{-4} M solution in THF of lithium tetracyanoethylene whose $g = 2.00270 \pm 0.00005$ and $A_N = 1.574$.

We have observed in the unlabeled TCNQ⁻ spectrum two sets of low intensity lines. One set arises from C^{13} at position 9. The other with one-half the signal intensity of that arising from position 9 has a splitting of 4.6 oersted. If the latter is due to C^{13} splitting, it must arise from the methylene carbons (*i.e.*, 7, 8). We have been unable to observe any other resonances in the unlabeled TCNQ⁻ spectrum.

Table I shows that the C^{13} splitting constants for positions 1 and 9 differ from those previously assigned⁴ and from those calculated from theory. The difference is even more pronounced if the value of 4.6 oersted can be associated with the C^{13} splitting by position 7. One concludes that either (perhaps both) the current theory of C^{13} hyperfine splitting or spin-density calculation is inadequate and requires revision.

The two C^{13} enriched TCNQ anion radicals were synthesized as follows. For TCNQ enriched by C^{13} in position 1 (4) (Scheme I), ethyl β -iodopropionate was treated with potassium cyanide- C^{13} to give β -ethoxycarbonyl propionitrile-1- C^{13} (I). Treatment of



I with ethanolic hydrogen chloride gave diethyl succinate-1- C^{13} which was treated with sodium ethoxide in ether to give 2,5-bis(ethoxycarbonyl)-1,4-cyclohexanedione- C^{13} which was hydrolytically decarboxylated to 1,4-cyclohexanedione-1(4)- C^{13} . The C^{13} -labeled cyclohexanedione was converted to TCNQ-1(4)- C^{13} and LiTCNQ-1(4)- C^{13} by the usual procedures.^{5,6} Mass spectral analysis of CO_2 result-

(5) D. S. Acker and W. R. Hertler, *J. Am. Chem. Soc.*, **84**, 3370 (1962).

(6) L. R. Melby, R. J. Harder, W. R. Hertler, W. Mahler, R. E. Benson, and W. E. Mochel, *ibid.*, **84**, 3374 (1962).

ing from combustion of the labeled TCNQ gave a value for C^{13}/C^{12} corresponding to $\sim 5\%$ C^{13} in each of positions 1 and 4, in excellent agreement with the expected value as well as with the relative e.s.r. line amplitudes.

TCNQ enriched by C^{13} in position 9 (11, 13, 15) was prepared by the reaction of potassium cyanide- C^{13} with TCNQ to give K^+TCNQ^- 9(11, 13, 15)- C^{13} which was then oxidized to the correspondingly labeled TCNQ.⁷ Mass spectral analysis again gave a value for C^{13}/C^{12} corresponding to $\sim 5\%$ C^{13} in each of the positions, in good agreement with relative e.s.r. line amplitudes.

(7) This method of labeling is analogous to that used in the preparation of cyano-labeled tetracyanoethylene- C^{13} [O. W. Webster, W. Mahler, and R. E. Benson, *ibid.*, **84**, 3678 (1962)].

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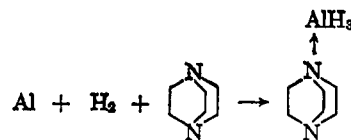
M. T. JONES
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RECEIVED FEBRUARY 1, 1964

The Direct Synthesis of Amine Alanes

Sir:

In previous papers we have reported the use of the Al-H₂ reducing system for the synthesis of NaAlH₄^{1,2} and amine boranes.³ Now we wish to report the first successful direct synthesis of an amine alane, triethylenediamine alane, by reaction of aluminum and hydrogen in the presence of triethylenediamine at moderate temperature and pressure.



In a typical experiment 30 g. of triethylenediamine was dissolved in 100 ml. of tetrahydrofuran. To this solution was added approximately 6 g. of activated aluminum powder.² The resulting mixture was heated for 6 hr. at 70° and 5000 p.s.i. hydrogen pressure. A light gray solid was isolated by filtration and analyzed for aluminum, hydrogen, and nitrogen. The nitrogen analysis was performed by potentiometric titration of the solution obtained on hydrolysis of the product, after removal of the Al(OH)₃. *Anal.* Calcd. for C₆H₁₂N₂·AlH₃: Al, 19.0; N, 19.7; H, 21.2 mmoles/g. Found: Al, 21.8; N, 19.1; H, 22.4 mmoles/g.

Deuterolysis of the product showed that 92.4% of the evolved gas was DH and 7.6% was D₂, indicating a low concentration of unreacted aluminum. The product is thermally stable to >200° and reacts violently with water. It is insoluble in the common organic solvents tested and for this reason no molecular weight determination has been made. However, it is speculated that the product is not monomeric, because of the difunctional nature of the amine. The ready formation

(1) E. C. Ashby (to Ethyl Corp.), French Patent 1,235,680 (May 30, 1960).

(2) E. C. Ashby, *Chem. Ind.* (London), 208 (1962).

(3) E. C. Ashby and W. E. Foster, *J. Am. Chem. Soc.*, **84**, 3407 (1962).

of this amine alone 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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E. C. ASHBY

RECEIVED MARCH 5, 1964

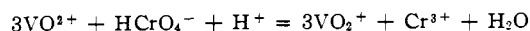
Oxidation of Vanadium(IV) by Chromium(VI) in Acidic Solution¹

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 absorptivity index of 140.6 l. mole⁻¹ cm.⁻¹. At the single acidity used in these studies, 0.00500 *F* HClO₄, the absorptivity 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 HCrO₄⁻; vanadium(IV),³ vanadyl ion VO²⁺; and vanadium(V),⁴ pervanadyl ion VO₂⁺.

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



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 Cr³⁺, 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

$$-d[\text{HCrO}_4^-]/dt = k[\text{VO}^{2+}]^2[\text{HCrO}_4^-]/[\text{VO}_2^+] \quad (1)$$

Precise linearity of an integrated form⁵ 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.

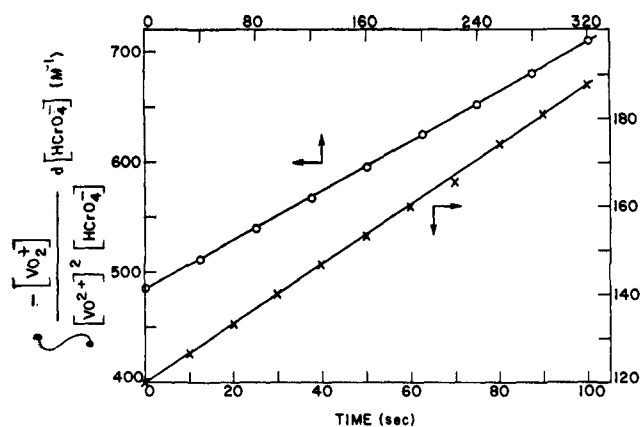


Fig. 1.—Linear plots of the integrated form⁵ of eq. 1 illustrating conformity to the rate law given. The two runs shown are expt. no. 4 (O) and 5 (X) in Table I.

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.

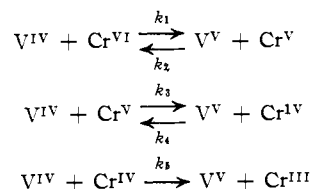
TABLE I
EXPERIMENTALLY DETERMINED VALUES^a OF THE RATE
CONSTANT *k*

Expt. no.	Initial concentrations × 10 ⁴ (<i>F</i>)— [Cr(VI)]	[V(V)]	[V(IV)]	Extent of reaction followed (%)	<i>k</i> (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* HClO₄, *I* = 1.00 *F* (with LiClO₄).

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: $k_{\text{Fe}}[\text{Fe}^{2+}]^2[\text{HCrO}_4^-]/[\text{Fe}^{3+}]$ and $k_{\text{Ce}}[\text{Ce}^{\text{IV}}]^2[\text{Cr}^{3+}]/[\text{Ce}^{\text{III}}]$, respectively. These rate law forms are the exact analogs of the present findings. Thus the apparent mechanism for this three-equivalent change is



(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).