Tetrahedron Letters,Vol.24,No.32,pp 3299-3302,1983 0040-4039/83 $3.00 + .00
Printed in Great Britain

CARBON-CARBON BOND FORMATION BY COORDINATION OF CARBOCATIONS WITH CARBANIONS.

Edward M. Arnett* and
E. B. Troughton

Department of Chemistry
Duke University
Durham, North Carolina 27706

Direct attack of resonance-stabilized carbenium ions and carbanions can be regulated to provide a wide range of rates and equilibria for the study of carbon-carbon bond formation.

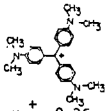
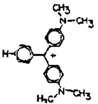
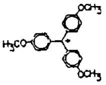
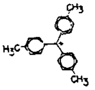
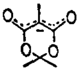
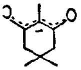
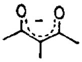
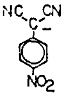
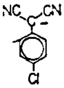
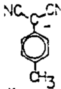
The simplest of all polar synthetic reactions should be that between carbenium ions and carbanions. Such a process should be valuable for studying the structure-reactivity behavior of electrophiles and nucleophiles since covalent bond formation is not complicated by the expulsion of a leaving group. Although carbenium ions and carbanions are usually considered to be very reactive intermediates, there are many familiar charge-delocalized examples of both types which are stable in the same region of the pH scale. It should be feasible to examine conveniently the kinetics of carbenium ion-carbanion coordination and, if both species are stabilized sufficiently, the covalent and ionic mixture could be equilibrated so that the kinetics and thermodynamics of bond formation could be studied.

Ample support for the feasibility of such rate and equilibrium studies of carbocation-anion reaction may be cited (1-4) using inorganic anions and variously stabilized carbenium ions to yield ion pairs and covalent species. However, we have found no clear precedent for the work presented here using reaction of a graded series of carbanions and carbenium ions.

Table I reports qualitative rate observations for the bleaching of tetrafluoroborate salts of crystal violet, malachite green and tropylium ion by lithium and potassium salts of four enolates of varying basicity and (presumably) nucleophilicity. These reactions confirmed a wide range of coordination rates which were reasonably related to the stabilities of both ions as expressed by the pK_Rs of the carbenium ions and the pK_as of the conjugate carbon acids of the enolates.

Table I.

Results of Reacting Cations and Carbanions in Solvents Shown at Room Temperature. COV = Covalent Coordination Product. Dimer = Dimerization Product from Radical of Carbanion

Carbocations Carbanions	 $pK_R^+ = 9.36$	 $pK_R^+ = 7.07$	 $pK_R^+ = 4.7$	 $pK_R^+ = 0.8$	 $pK_R^+ = -3.56$
 Na^+ $pK_{HA} = 10$	DMSO Ions persist for over one week	DMSO Ions persist for over one week	DMSO COV in seconds		
 Na^+ $pK_{HA} = 11.3$	DMSO COV in minutes	DMSO COV in seconds			
 Li^+ Na^+	d^6 DMSO 90% COV in 1 week by ^1H NMR COV in 30 minutes	COV in minutes COV in seconds	DMSO COV in seconds C-alkylation by ^1H NMR		
 Li^+ K^+ $pK_{HA} = 15.1$	DMSO COV in 20 seconds COV in 20 seconds				
 K^+	In $CD_3C{\equiv}N$ only Ions Detected by ^1H NMR after 6 months		In CD_3CN Ion COV equilibrium observed by ^1H NMR	Ions COV Equilibrium, Solvent Dependent	Dimer isolated
 K^+ $pK_{HA} = 3.14$			d^6 acetone COV		
 K^+ $pK_{HA} = 4.85$			MeOH Dimer	Acetone Dimer	

A quantitative examination of the reaction of crystal violet BF_4 (CV) with the lithium and potassium enolates of dipivaloylmethane in DMSO gave clean second order reactions by following the disappearance of the 602 nm. band of CV. The results indicate clearly the effect of the concentration and nature of the alkali cation as it affects ion-pairing of the enolate (5).

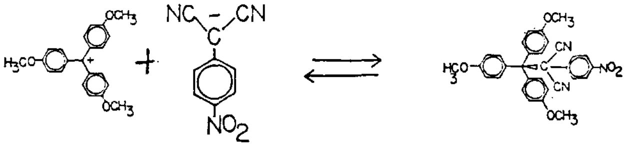
The activation parameters derived for reaction of CV with the potassium enolate ($\Delta H^{\neq}$=12.5 ± 0.7 kcal/mole, $\Delta S^{\neq}$=-18.2 gibbs/mole) can be compared with Ritchie's values (2) for reaction of CV with cyanide ion in water at 25° ($\Delta H^{\neq}$=14.8 kcal/mole $\Delta S^{\neq}$=-15 gibbs/mole.

It was more difficult to find a system that yielded an equilibrium mixture of free ions or ion-pairs and a neutral covalent product with clean formation of a carbon-carbon bond. Since enolates are ambident nucleophiles we chose substituted phenylmalononitrile salts as a series of carbanions which were more likely to react at carbanion carbon (6) and which could also provide a series of m- and p-substituted ions for structure-reactivity studies. Since triarylmethyl cations can suffer attack on the benzene rings as well as the central carbon (7) we also tried tropylium and substituted cyclopropenium ions.

Table I indicates that other reaction channels are available in addition to the originally proposed coordination route. Thus, electron transfer appeared to be involved in several cases as manifested by the precipitation of the geminate product from the radical of the anion. Redox potentials of separate solutions of cations and anions could be examined and also of some mixtures. Thus, the quantitative relationships between carbon-carbon bond formation through coordination and electron transfer channels may be compared. There is also precedent for the formation of charge-transfer complexes (8).

The equilibrium between trianisylmethyl cation and nitrophenylmalononitrile anion with their covalent product could be monitored by NMR and was clearly dependent on the polarity of the medium, as might be expected (Table II).

Table II. Solvent Effect on an Ion $\rightleftharpoons$ Covalent Equilibrium



Solvent (ε)*	% Ions	%Covalent
CD_2Cl_2 (8.93)	70	30
CD_3CN (37.5)	45	55
d^6 acetone (20.7)	15	85
d^8 THF (7.58)	0	100
d^8 THF (added CD_3CN)	5	95
Ligroine/CH_2Cl_2	Anion Dimer Isolated	

*Dielectric constants for undeuterated solvents.

In summary, we have demonstrated that the reactions of resonance-stabilized carbenium ions and carbanions should provide an excellent opportunity to study rates and equilibria for ion-pair and covalent bond formation through direct reaction between organic electrophiles and nucleophiles free of leaving groups. The relation between cation-anion charge annihilation and electron transfer should also be readily examined.

Acknowledgement - This work was supported by NSF Grant CHE-8006202 for which we are most appreciative. The stopped-flow kinetics apparatus was designed and built by Dr. G. W. Schriver.

References

1. H. Kessler and M. Feigel, Acc. Chem. Res., 15, 208, (1982).
2. C. D. Ritchie, D. J. Wright, D. Haung, and A. A. Kamaego, J. Am. Chem. Soc., 97, 1163, (1975).
3. M. E. Volpin, I. S. Akhrem, and D. N. Kursanov, Zh. Obshch. Khim., 28, 330, (1958).
4. J. Hine, J. Am. Chem. Soc., 93, 3701, (1971).
5. V. M. DePalma and E. M. Arnett, J. Am. Chem. Soc., 100, 3514, (1978).
6. H. D. Hartzler, J. Am. Chem. Soc., 86, 2174, (1964).
7. H. E. Zaugg, R. J. Michaels, and E. J. Baker, J. Am. Chem. Soc., 90, 3800, (1968).
8. E. LeGoff and R. B. LaCount, J. Am. Chem. Soc., 85, 1354, (1963).

(Received in USA 10 May 1983)