Cross Hydrodimerization of Acrylonitrile, Ethyl Acrylate, and Methacrylonitrile by Sodium Amalgam

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Abstract: The reaction of acrylonitrile (M_1), ethyl acrylate (M_2), and methacrylonitrile (M_3) with Na amalgam was studied in solvent systems, DMSO–diglyme and liquid ammonia. It was found that when phenol was used as proton donor the homo hydro dimers and the cross hydro dimers of these monomers were obtained. It was thus possible to measure relative rate constants for the electron-transfer reactions $\mathrm{Na(Hg)} + \mathrm{M(solvent)} \rightarrow \mathrm{Na^+(solvent)\,M\cdot^-}$, the reaction of the radical anion with itself $M_1\cdot^- + M_1 \rightarrow \cdot M_1M_1^-$, and the cross reaction of the radical anion with another monomer $M_1\cdot^- + M_2 \rightarrow \cdot M_1M_2^-$. The following relative rate constants were measured: electron transfer (DMSO) $k'_1/k'_2 = 0.6$, $k'_1/k'_3 = 120$, and $k'_2/k'_3 = 200$; (liquid NH_3) $k'_1/k'_2 = 0.7$, $k'_1/k'_3 = 3$, and $k'_2/k'_3 = 4.5$; cross hydrodimerization (DMSO) $k_{11}/k_{12} = 0.7$, $k_{22}/k_{21} = 0.3$, $k_{11}/k_{13} = 3.5$, and $k_{22}/k_{23} = 1.2$; (liquid NH_3) $k_{11}/k_{12} = 0.8$ and $k_{22}/k_{21} = 0.4$.

In previous publications[2,3] we have reported studies on the reactions of acrylonitrile (AN) and methacrylonitrile (MeAN) with Na amalgam. It was shown that in solvent systems such as dimethyl sulfoxide (DMSO) or liquid NH_3 one can obtain mainly the corresponding hydro dimers. The work was now extended to mixtures of monomers where cross hydrodimerization takes place. Previous work in cross electrochemical coupling has been done by Baizer,[4] Wiemann,[5] and Matsuda.[6] Their emphasis however, was on the synthetic applications of the method and no quantitative data were reported. In the present study we have treated the subject in a quantitative form and we have derived relative rate constants for the elementary steps of reaction of radical ions and monomers.

Experimental Section

In order to study the kinetics of a heterogeneous reaction one has to control the degree of dispersion of the two phases. This will depend on the physical characteristics of the reactor, the rate of stirring, and the volumes of the two phases. This problem was discussed in an earlier publication.[2] In the present work we have followed the same standard technique as described previously. The reaction vessel used was a round-bottomed flask with an exit tube at the bottom. The flask was equipped with a stirrer connected to a revolutions-per-minute counter and to an electric stop watch. In every experiment 45 cc of Na amalgam (0.7–1.5 *M* Na) and 20 cc of solution were used. Two solvents used were (1) 50% w/v of DMSO in diglyme and (2) liquid ammonia. In both cases phenol was used as a proton donor. Its concentration was equal to that of the sum of monomers used. In liquid ammonia only the hydro dimers were produced, while in DMSO–diglyme solutions, some hydrogenated monomers were also found—3% propionitrile (PN) from AN and 7% ethyl propionate (EP) from ethyl acrylate. These were minor side products which would not interfere seriously with the hydrodimerization studied. The reaction time in all cases was constant, $t = 10$ sec. The rate of stirring was kept at 400 rpm for DMSO and 250 rpm for NH_3. This resulted in about 30% conversion in both solvents. The reaction temperatures were 0 and −40° for DMSO and NH_3, respectively. The reproducibility of the system was checked and the experimental error was found to be about 10%.

The monomers, M_1 (acrylonitrile, AN), M_2 (ethyl acrylate, EA), and M_3 (α-methyl acrylonitrile, MeAN), were distilled before use. Diglyme was dried over CaH_2 and DMSO over molecular sieves. They were both distilled under vacuum. Liquid ammonia, pure grade, was used without further purification. Phenol was analytical grade. The products of the reaction were determined by gas chromatography.

Results and Discussion

1. Cross Hydrodimerization of AN and EA. As reported previously[2] the reaction is first order with respect to monomer. This was verified again, for each monomer separately, in both solvent systems used. The results for DMSO–diglyme solution are presented in Table I and for liquid ammonia solution in Table II. The homo hydro dimers obtained from AN and EA are adiponitrile (ADN) and ethyl adipate (EAD), respectively. It can be seen that in both cases the per cent conversion (at constant time, $t = 10$ sec) is independent of concentration for the range used in our study. It was also shown[2] that the reaction is first order with respect to the Na concentration in the amalgam. The rate-determining step, as previously established, is

$$\mathrm{Na} + \mathrm{M(solvent)} \xrightarrow{k'} \mathrm{Na^+(solvent)M\cdot^-} \qquad (1)$$

The product is a solvent-separated ion pair, but for

Table I. Dependence of the Rate of Homo Hydrodimerization on the Initial Concentrations of AN and EA in DMSO–Diglyme Solution

$[AN]_0$, mmol	[PN], mmol	[ADN], mmol	% PN	% ADN
1.06	0.01	0.13	0.9	25.0
2.02	0.013	0.26	0.6	26.0
2.61	0.021	0.34	0.8	26.0
3.15	0.031	0.39	1.0	25.0
6.0	0.049	0.60	0.8	20.0
$[EA]_0$, mmol	[EP], mmol	[EAD], mmol	% EP	% EAD
1.02	0.028	0.18	2.8	35.0
1.10	0.033	0.19	3.0	35.0
2.50	0.05	0.43	2.0	35.0
3.06	0.05	0.50	1.6	33.0
4.03	0.065	0.66	1.6	33.0
4.05	0.069	0.69	1.7	34.0
5.0	0.08	0.71	1.6	29.0

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(1) Taken in part from the Ph.D. thesis of H. Rosen to be presented to the Scientific Council of the Weizmann Institute of Science.

(2) Y. Arad, M. Levy, H. Rosen, and D. Vofsi, *J. Polymer Sci., A-1,* in press.

(3) Y. Arad, M. Levy, H. Rosen, and D. Vofsi, *ibid., B,* in press.

(4) M. M. Baizer, *J. Org. Chem.,* **29,** 1670 (1967).

(5) J. Wiemann and M. L. Bouguerra, *Compt. Rend.,* **265,** 751 (1967).

(6) F. Matsuda, *Tetrahedron Letters,* 6193 (1966).

Table II. Dependence of the Rate of Homo Hydrodimerization on the Initial Concentrations of AN and EA in Liquid NH_3 Solution

$[AN]_0$, mmol	[ADN], mmol	% ADN
1.02	0.15	29
1.06	0.14	26
1.9	0.19	20
1.9	0.19	20
1.9	0.22	23
2.9	0.40	28
2.9	0.35	24
3.8	0.49	26
5.7	0.71	25
5.7	0.74	26
7.5	0.93	25
$[EA]_0$, mmol	**[EAD], mmol**	**% EAD**
1.0	0.15	30
1.0	0.17	34
2.0	0.29	29
4.0	0.60	30
6.0	1.10	37
8.0	1.30	33

simplicity we shall refer to it as $M\cdot^-$. The reactions following this step, namely, dimerization, a second electron transfer, and protonation, are faster and therefore not rate determining. As the two monomers were studied under identical conditions we can calculate the relative rates for the electron transfer reaction. It is $(k'_1/k'_2)_{DMSO} = 0.6$ and $(k'_1/k'_2)_{NH_3} = 0.7$. (The reactions leading to the hydrogenated monomers were not considered in these calculations.) In both cases EA is more reactive than AN; the nature of the solvent and the difference in temperature seems to have very little effect on the ratio. We then proceeded to study monomer mixtures. The ratio of monomers was varied by a factor of 16. The products consisted of the two homo hydro dimers and the cross hydro dimer ethyl cyanovalerate (ECV). The results are presented in Tables III and IV.

The general scheme for any two monomers involves eq 2–5.

$$M_1\cdot^- + M_1 \xrightarrow{k_{11}} \cdot M_1M_1^- \longrightarrow (M_1H)_2 \qquad (2)$$

$$M_1\cdot^- + M_2 \xrightarrow{k_{12}} \cdot M_1M_2^- \longrightarrow (HM_1M_2H)_{M_1\cdot^-} \qquad (3)$$

$$M_2\cdot^- + M_2 \xrightarrow{k_{22}} \cdot M_2M_2^- \longrightarrow (M_2H)_2 \qquad (4)$$

$$M_2\cdot^- + M_1 \xrightarrow{k_{21}} \cdot M_1M_2^- \longrightarrow (HM_1M_2H)_{M_2\cdot^-} \qquad (5)$$

In order to calculate the rate constants one could apply the steady-state approximation for the two radical ions. We have tried to calculate k_{11}/k_{12} and k_{22}/k_{21} from the resulting expression but were unable to obtain any reasonable results. This is probably due to the fact that the two radical ions involved are independent and are not related by a single expression as in the case of copolymerization. We have, therefore, tried another approach.

k_{11}/k_{12} and k_{22}/k_{21} can be obtained by dividing eq 2 by 3 and 4 by 5, respectively

$$\frac{[ADN]}{[ECV]_{AN\cdot^-}} = \frac{k_{11}[AN]}{k_{12}[EA]} \qquad (6)$$

$$\frac{[EAD]}{[ECV]_{EA\cdot^-}} = \frac{k_{22}[EA]}{k_{12}[AN]} \qquad (7)$$

where $[ECV]_{AN\cdot^-}$ represents the amount of the cross hydro dimer obtained by reaction 3 from $AN\cdot^-$ while $[ECV]_{EA\cdot^-}$ represents that obtained by reaction 5 from $EA\cdot^-$. These values can be calculated from eq 8 and 9 where $[ADN]_0$ and $[EAD]_0$ represent the amounts

$$[ECV]_{AN\cdot^-} = [ADN]_0 - [ADN] \qquad (8)$$

$$[ECV]_{EA\cdot^-} = [EAD]_0 - [EAD] \qquad (9)$$

of homo hydro dimers obtained in the control homodimerization experiments with the corresponding concentrations of each monomer separately, while [ADN] and [EAD] represent the amounts found in the cross hydrodimerization experiment with the mixture of monomers. These expressions would be true provided the electron transfer to each monomer is not influenced by the presence of the second monomer. In other words, the sum of all the hydrodimers in a cross hydrodimerization experiment (referred to as Σ_{dimers} (exptl) in Tables III and IV) should be equal to the sum of the homo hydro dimers in the two control experiments with each monomer separately (Σ_{dimers} (calcd)). This can be verified from the last two columns in Tables III and IV. We are justified therefore in using these expressions for calculating the ratio of rate constants. The values of [AN]/[EA] used in the calculations were the averages between initial and final values. As the conversions were about 30% this should not introduce a considerable error. The calculated values are given in Tables V and VI. One can see that the results are somewhat scattered, and in some cases there is a trend. However, considering the experimental difficulties and the indirect method used for the calculation, one may consider these values as reasonable estimates for the rate constants.

One should also consider the possibility of fast electron transfer between the radical ions and monomers

$$AN\cdot^- + EA \overset{K}{\rightleftharpoons} AN + EA\cdot^-$$

which should yield the expressions

$$\frac{[ADN]}{[EAD]} = K\frac{k_{11}}{k_{22}}\left(\frac{[AN]}{[EA]}\right)^2$$

and

$$\frac{[ADN]}{[ECV]} = \frac{k_1}{K(k_{12} + k_{21})}\left(\frac{[AN]}{[EA]}\right)$$

Both expressions are not in agreement with our experimental results. The reason for this may be due to the fact that the reaction does not take place in the bulk of the solution but on the mercury interface where the diffusion is much more restricted. Rapid exchange can probably take place, but before the molecule and the radical ion can diffuse away from each other, they will interact again and addition will occur. Moreover, the dimeric ion radical formed will still remain in the double layer to acquire another electron before it can diffuse out and be protonated. However, there may be some cases where such an exchange

Table III. Cross Hydrodimerization of AN and EA in DMSO–Diglyme

$([AN]/[EA])_0$	$[AN]_0$, mmol	$[EA]_0$, mmol	[ADN], mmol	[EAD], mmol	[ECV], mmol	Σ_{dimers}, mmol	
						Expt	Calcd
4.0	4.04	1.04	0.39	0.0085	0.29	0.69	0.68
3.0	3.08	1.02	0.27	0.011	0.28	0.56	0.55
2.0	2.11	1.06	0.17	0.018	0.30	0.49	0.44
1.0	1.0	1.0	0.055	0.042	0.24	0.34	0.29
1.0	2.03	2.03	0.094	0.063	0.44	0.60	0.59
1.0	2.58	2.55	0.132	0.098	0.62	0.85	0.75
0.5	1.04	2.04	0.03	0.16	0.36	0.55	0.47
0.33	1.0	3.00	0.014	0.27	0.35	0.63	0.62
0.25	1.05	4.00	0.007	0.37	0.36	0.74	0.79

Table IV. Cross Hydrodimerization of AN and EA in Liquid Ammonia Solution

[AN]/[EA]	$[AN]_0$, mmol	$[EA]_0$, mmol	[ADN], mmol	[EAD], mmol	[ECV], mmol	Σ_{dimers}, mmol	
						Exptl	Calcd
3.8	3.8	1.0	0.39	0.007	0.22	0.61	0.63
2.00	8.0	4.0	0.62	0.045	0.84	1.51	1.64
1.90	1.9	1.0	0.15	0.01	0.23	0.39	0.40
1.45	5.8	4.0	0.37	0.08	0.79	1.16	1.36
1.45	5.7	4.0	0.40	0.08	0.89	1.37	1.35
1.00	1.0	1.0	0.04	0.033	0.23	0.30	0.29
0.93	2.8	4.1	0.20	0.17	0.93	1.30	1.13
0.93	1.9	2.0	0.11	0.075	0.43	0.62	0.56
0.93	2.9	2.0	0.10	0.085	0.47	0.66	0.68
0.93	3.8	4.1	0.17	0.14	0.84	1.15	1.13
0.95	3.8	4.0	0.17	0.13	0.78	1.08	1.11
0.71	2.9	4.0	0.12	0.28	0.83	1.23	1.00
0.70	2.8	4.0	0.10	0.22	0.76	1.08	1.01
0.50	2.0	4.0	0.05	0.28	0.57	0.90	0.89
0.31	1.9	6.0	0.025	0.73	0.77	1.53	1.20
0.24	1.9	8.0	0.04	0.94	0.74	1.72	1.52

Table V. Calculated Rate Constants for Cross Hydrodimerization of AN and EA in DMSO–Diglyme

[AN]/[EA]	$[ADN]/[ECV]_{AN\cdot^-}$	k_{11}/k_{12}	$[EAD]/[ECV]_{EA\cdot^-}$	k_{22}/k_{21}
4.0	3.4	0.85	0.053	0.21
3.0	2.3	0.77	0.07	0.21
2.0	1.8	0.90	0.115	0.23
1.0	0.78	0.78	0.34	0.34
1.0	0.59	0.59	0.23	0.23
1.0	0.70	0.70	0.31	0.31
0.5	0.30	0.60	0.94	0.47
0.33	0.13	0.40	1.2	0.40
0.25	0.054	0.22	1.3	0.32

Table VI. Calculated Rate Constants for AN and EA in Liquid NH_3

$([AN]/[EA])_0$	$[ADN]/[ECV]_{AN\cdot^-}$	k_{11}/k_{12}	$[EAD]/[ECV]_{EA\cdot^-}$	k_{22}/k_{21}
3.8	4.9	1.3	0.045	0.17
2.0	1.6	0.8	0.082	0.16
1.45	1.1	0.76	0.15	0.23
1.0	0.4	0.4	0.25	0.25
0.93	0.74	0.80	0.35	0.33
0.70	0.53	0.76	0.73	0.51
0.50	0.25	0.50	0.78	0.39
0.31	0.15	0.48	1.95	0.60
0.24	0.20	0.84	2.70	0.64

will be more important and it may lead to a situation where the amount of homo dimer will increase as a result of addition of the second monomer. An indication of such behavior was found in one of our studies and a complete report will be published in the future.

2. Cross Hydrodimerization of MeAN with AN and EA. MeAN should prove to be a simpler case as it was shown (ref 2) that its rate of reaction with Na amalgam is about 100 times slower than AN or EA when the solvent is DMSO–diglyme. Consequently, when the reaction is carried out with MeAN alone under the same experimental conditions, practically no homo hydro dimer can be detected. We can conclude, therefore, that in cross hydrodimerization of MeAN with AN only the radical ion $AN\cdot^-$ is formed and the products are ADN and the cross hydro dimer methyl adiponitrile (MeADN). The ratio of the hydro dimers will therefore be given by eq 2 and 3

Table VII. Cross Hydrodimerization of AN and MeAN in DMSO–Diglyme

([AN]/[MeAN])	$[AN]_0$, mmol	$[MeAN]_0$ mmol	[MeADN] mmol	[ADN], mmol	[ADN]/[MeADN]	k_{11}/k_{13}
...	4.0	0	...	0.45	...	...
6.9	4.0	0.58	0.018	0.40	22.2	3.5
4.1	4.1	1.0	0.034	0.43	12.6	3.4
2.0	4.0	2.0	0.056	0.39	7.0	3.8
1.0	4.0	4.0	0.105	0.39	3.7	4.1
0.5	4.1	8.0	0.174	0.35	2.0	4.3

$$\frac{[ADN]}{[MeADN]} = \frac{k_{11}}{k_{13}}\left(\frac{[AN]}{[MeAN]}\right) \tag{10}$$

For MeAN and EA the hydro dimers are formed from the radical ion $EA\cdot^-$, giving EAD and 2-methyl ethyl

Table VIII. Cross Hydrodimerization of EA and MeAN in DMSO–Diglyne

[EA]/[MeAN]	$[EA]_0$, mmol	$[MeAN]_0$, mmol	[MeEVC], mmol	[EAD], mmol	[EAD]/ [MeECV]	k_{22}/k_{23}
...	4.0	0	...	0.66	...	...
7.9	4.0	0.51	0.107	0.56	5.3	0.7
4.1	4.0	0.98	0.14	0.57	4.1	1.1
1.9	4.0	2.08	0.23	0.53	2.3	1.3
1.0	4.05	4.06	0.37	0.41	1.1	1.2
0.5	4.0	8.1	0.32	0.28	0.87	1.9

cyanovalerate (MeECV). The ratio of rate constants is given by the corresponding equation

$$\frac{[EAD]}{[MeECV]} = \frac{k_{22}}{k_{23}}\left(\frac{[EA]}{[MeAN]}\right) \qquad (11)$$

As in the previous case the values for the ratio of monomers in the equations were taken as averages between the initial and final values.

The experimental data are presented in Tables VII and VIII for AN and EA, respectively. One can see that the values of k_{11}/k_{13} and k_{22}/k_{23} are reasonably constant with some increasing trend. This trend may be due to some other side reaction which is affected by the presence of the second monomer.

The behavior of MeAN in liquid ammonia is rather unusual. It has a high rate of reaction with amalgam $k'_1/k'_3 = 3$, and does not behave in a regular form in cross hydrodimerization reactions. Further work on this problem is in progress.

Conclusions

In this work we have used Na amalgam as a readily available source of Na to yield radical ions of electronegative monomers. The ions are formed in the presence of a weak proton donor such as phenol. This enables us to measure relative rate constants for the electron transfer reaction and for the reaction of addition of monomers to the respective radical anions. The average values of the constants obtained are summarized in Table IX. One can deduce from the results in DMSO that EA is more electronegative than AN as reflected by k'_1/k'_2. The radical ion $AN\cdot^-$ reacts almost equally with AN and EA while it reacts slower with MeAN as could be expected. $EA\cdot^-$, on the other hand, reacts almost equally with MeAN and EA while it reacts slower with AN. This is rather unexpected. Interpretation of these results should await data from a number of other monomers and comparison of the rates of radical ions with the rates of the corresponding carbanions. The results in liquid ammonia, for AN and EA, are very similar to those in DMSO. The outstanding result, however, is the large increase in rate of electron transfer to MeAN in liquid ammonia compared to DMSO. This factor makes liquid ammonia an interesting solvent for electrochemical coupling reactions and should instigate further study.

Table IX. Rate Constants Measured for AN, EA, and MeAN in DMSO and Liquid NH_3

	DMSO	Liquid NH_3
	[AN]/[EA]	
k'_1/k'_2	0.6	0.7
k_{11}/k_{12}	0.7	0.8
k_{22}/k_{21}	0.3	0.4
	[AN]/[MeAN]	
k'_1/k'_3	120	3
k_{11}/k_{13}	3.5	...
	[EA]/[MeAN]	
k'_2/k'_3	200	4.5
k_{22}/k_{23}	1.2	...

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