The Autoxidation of Alkylnitroaromatic Compounds in Base-catalysed Phase-transfer Catalysis by Polyethylene Glycol under Ultrasonic Radiation

Ronny Neumann and Yoel Sasson*

Casali Institute of Applied Chemistry, School of Applied Science and Technology, The Hebrew University of Jerusalem, 91904 Jerusalem, Israel

The use of ultrasonic agitation in the base-catalysed autoxidation of alkylnitrobenzenes in polyethylene glycol phase-transfer systems changes reaction selectivity from the usual dimeric products to the carboxylic acid.

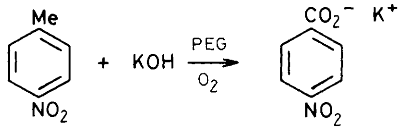
Recently, the use of ultrasonic irradiation in synthetic organic chemistry as a method of agitating heterogeneous reaction systems has rapidly gained recognition. Among its first uses were in cleansing the surface of catalysing metals in such reactions as the cyclopropanation of alkenes using the Simmons–Smith reagent,[1] the debromination of α-bromoketones using mercury,[2] and the preparation of Grignard[3] or organozinc reagents.[4] More recent uses have been in the basic alumina-catalysed alcohol condensation of ketones[5] and the cyanation of acyl chlorides,[6] and in phase-transfer catalysis systems, in the *N*-alkylation of amines[7] and the alkylation of a Reissert compound.[8] Generally, greatly increased reaction rates and yields have resulted.

We now report the use of ultrasonic irradiation in the base-catalysed autoxidation of alkylnitrobenzenes, such as *p*-nitrotoluene, to give the corresponding nitrobenzoic acids. We have used a phase-transfer system with polyethylene glycol (PEG) as a catalyst [reaction (1)]. Previously, we used the usual mechanical agitation in a similar autoxidation of weak carbon acids,[9] but attempts to perform reaction (1) using mechanical agitation yielded *only* dimeric products [reaction (2)].

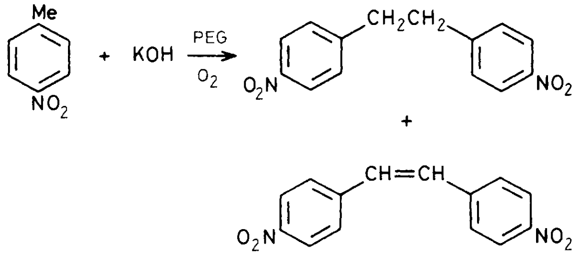
The results of the original autoxidation of this type performed in a homogeneous reaction medium[10] indicated that two methods could increase the yield of the carboxylic acid at the expense of the dimer: very low concentrations (<0.1 M) or high oxygen concentrations (pressure) could be used. Our attempts to use these principles in heterogeneous phase-transfer catalysis to increase yields of the carboxylic acid failed whereas a combination of phase-transfer catalysts and ultrasonic agitation gave surprising results.

The results of our experiments are in Table 1. When using mechanical stirring (expts. 1—7) only dimeric products were found. Increasing the oxygen pressure (expt. 4) or decreasing the substrate concentration (expt. 3) had no effect on the overall selectivity albeit affecting the overall yield. All the substrates (expts. 2, 5—7) underwent the same reaction, the *para*-position being more active probably owing to steric reasons whereas methyl groups were slightly more active than the ethyl side chains.

When using ultrasonic agitation significantly different results were obtained in one-third the reaction time. First it is important to note that the phase-transfer catalyst is a necessary component even under ultrasonic agitation (expt. 12). Secondly, for the *para*-substituted compounds (expts. 8,10) the yields were greatly *increased* compared with those for mechanical agitation conditions (expts. 2,7). In addition, significant amounts of carboxylic acid were formed, the ethyl



(1)



(2)

Table 1. The base-catalysed autoxidation of alkylnitrobenzenes under phase-transfer conditions.

		Yield, mol %[c]		
Expt.	Substrate[b]	Carboxylic acid	Dimer	Catalyst
Mechanical agitation[a]				
1	PNT	0	5.4	PEG-6000[j]
2	PNT	0	26.8	PEG-400
3	PNT[d]	0	19.3	PEG-400
4	PNT[e,f]	0	38.7	PEG-400
5	ONT	0	18.1	PEG-400
6	OENB	0	17.2	PEG-400
7	PENB	0	22.0	PEG-400
Ultrasonic agitation[a]				
8	PNT	21.1	34.9	PEG-400
9	ONT	1.6	2.4	PEG-400
10	PENB	22.2	5.8	PEG-400
11	OENB	0.5	1.3	PEG-400
12	PNT	0	0	None
13	PNT	10.3	14.5	PEG-400 BZE[g]
14	PNT	5.6	7.7	PEG-6000[j]
15	PNT	14.6	27.2	TBAHS[h]
16	PNT[d]	43.1	2.3	PEG-400
17	PNT[i]	16.7	17.1	PEG-400

[a] Reaction conditions: mechanical agitation, 0.01 mol of substrate, 0.05 mol of KOH, and 0.001 mol of catalyst in 10 ml of toluene under oxygen were mixed using a RZR-01 mechanical stirrer at 1500 r.p.m. at 25 °C for 3 h; ultrasonic agitation, 0.01 mol of substrate, 0.05 mol of KOH, and 0.001 of catalyst in 10 ml of toluene at 25 °C under oxygen were agitated in a Sonicor ultrasound bath for 1 h. [b] PNT = *p*-nitrotoluene, ONT = *o*-nitrotoluene, OENB = *o*-ethylnitrobenzene, PENB = *p*-ethylnitrobenzene. [c] Isolated yields. [d] 0.001 mol of PNT. [e] Under 75 psi of O_2. [f] Shaking in a Parr autoclave. [g] PEG-400 dibenzyl ether. [h] Tetrabutylammonium hydrogen sulphate. [i] NaOH instead of KOH. [j] 0.667 mmol.

side chain giving the best selectivity. On the other hand for *ortho*-substituted compounds (expts. 9,11) the yields were greatly *decreased* compared with those with mechanical agitation (expts. 5,6) although the increased selectivity was retained. From these results we conclude that the ultrasonic agitation inhibits the dimerization reaction while increasing the general reaction rate in the case of the *para*-substituted compounds, whereas in the *ortho*-substituted compounds the dimerization is likewise inhibited while the oxidation product is also inhibited in this case possibly for steric reasons. The use of different catalysts (expts. 13—15) and the use of NaOH (expt. 17) instead of KOH also had little effect on the selectivity. On the other hand a tenfold reduction in the concentration of the substrate (expt. 16) increased the selectivity significantly, the carboxylic acid being almost the sole product.

Received, 17th January 1985; Com. 075

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