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FURTHER EVIDENCE FOR THE EFFECT OF ULTRASONIC WAVES ON ELECTRON TRANSFER PROCESSES - THE CASE OF THE KORNBLUM-RUSSELL REACTION

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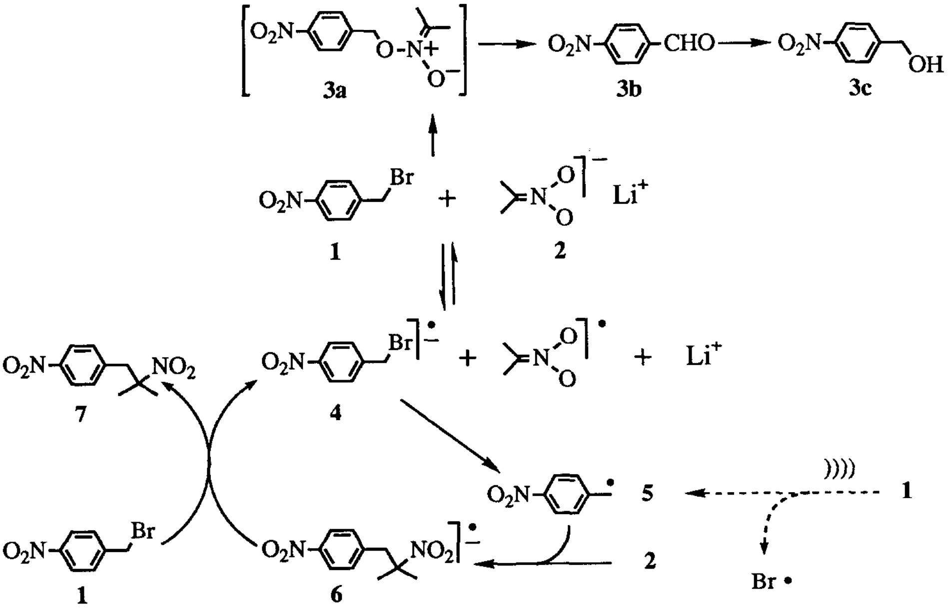
***Key Words:** Ultrasound; electron transfer; $S_{RN}1$ reaction.*

***Abstract:** The Kornblum–Russell reaction is directly influenced by sonication. Under optimal conditions of irradiation, the ratio of C/O alkylation is practically reversed with respect to that of the silent reaction, indicating a direct intervention of sonic waves in the electron transfer process.*

We recently proposed a new interpretation of sonochemical reactions, according to which sequential electron transfer processes are favoured by ultrasonic irradiation at the expense of polar (simultaneous bielectronic) ones.[1] We now wish to describe the recent results of a study of a homogenous reaction known to be able to follow both mechanisms — the Kornblum–Russell alkylation of nitronate anions.[2] The generally accepted mechanism is given in Scheme 1.



Scheme 1

Our experiments were performed with solvents and liquid reagents carefully dried and distilled under argon before use. A 0.01M ethanolic solution of 4–nitrobenzyl bromide (17 mL, 0.17 mmol) was injected under argon into a darkened reaction vessel) and subjected to ultrasound (30 kHz Ultrason Annemasse generator) whilst passing a stream of argon through it for 10-15 min. and adjusting the solution temperature to 12-13°C. A 1.0M solution of 2-lithio-2-nitropropane (0.19 mL, 0.19 mmol, obtained from 9.1 mL ethanol, 70 mg lithium and 0.89 g nitropropane) was injected and the mixture was sonicated for 7 h. Ethanol was removed under reduced pressure, the residue dissolved in ethyl acetate and the solution washed with brine, dried (Na_2SO_4) and the solvent evaporated. An aliquot was analysed by GLC (Carlo Erba, SE 30 10%, 2.5 m column, detector calibrated for the response factors with authentic samples). The remaining sample was treated with $NaBH_4$ to give a practically quantitative amount of the crude mixture.[3] Column chromatography led to compounds **1**, **3c** and **7**, the sum of which represented in most cases 80% of the maximum amount expected. The ratio of **7**:**3c** isolated in this manner was generally of the same order of magnitude as the **7**:**3b** GLC ratio. Several minor components were also formed but their individual yields were less than 2%.

Three sets of experiments were run: **A**, in the usual sonication vessel[4] with a 5mm diameter horn; **B**, in the vessel shown in Fig.1 with the same horn as in **A**; **C**, as in **B** with a 9.5 mm horn. In **B** and **C** the geometry was adjusted to obtain standing waves,[5] which were absent in **A**. In Fig. 2 the variations of the ratio **7**:**3c** have been represented as a function of sonic intensity.[6]

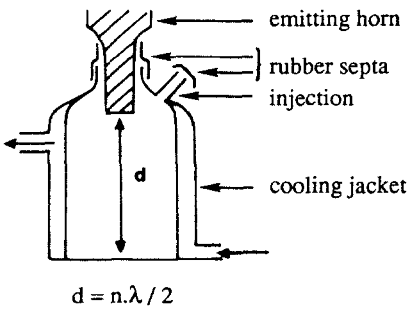


Fig. 1

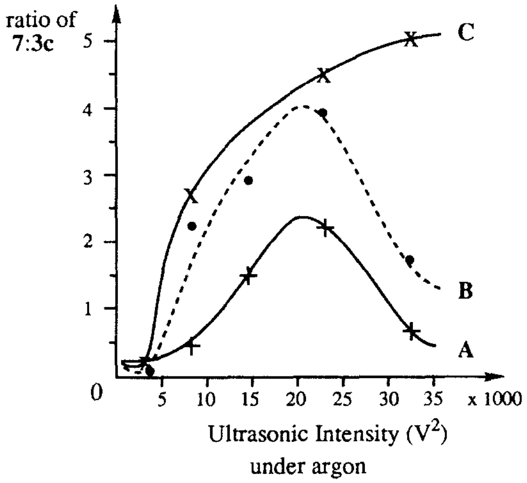


Fig. 2

In the absence of sonic waves the O-alkylation product is largely predominant and gives a ratio of **7**:**3b** = 0.1-0.2; a value that can be compared to that obtained from an experiment run with a sound intensity of $(150V)^2$ in the presence of air. In agreement with our predictions, the polar mechanism is not accelerated by sonication.

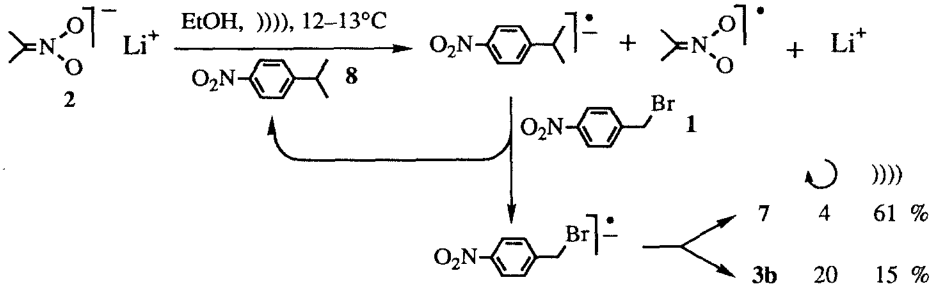
Table: Products isolated from the experiments under the three sets of conditions.

Conditions	A			B			C		
Product Yields (%) / Sound Intensity $(V)^2$	**1**	**3c**	**7**	**1**	**3c**	**7**	**1**	**3c**	**7**
0	12	60	13	—	—	—	—	—	—
$(50)^2$	—	—	—	70	16	3	61	13	3
$(90)^2$	9	57	21	18	18	41	35	13	34
$(120)^2$	2	32	46	32	15	43	—	—	—
$(150)^2$	1	23	48	17	16	62	30	11	45
$(180)^2$	2	44	29	30	35	21	15	10	49

Standing waves have an important effect upon the $S_{RN}1$ pathway. The importance of standing waves in sonochemical processes has already been alluded to[7] but it is not clear if reactions occur at the pressure nodes or antinodes. Standing waves seem to "gelify" the medium and the conversion yield suffers from this diminished diffusion of the reactants, especially at low intensities, where 60-70% of initial **1** is recovered. At higher intensities, the reaction zones become broader under the effects of radiation pressure,[8] the conversion yield increases to 70-85% and the C-alkylation reaction predominates. These observations converge to establish that the pathway proceeding via a sequential electron transfer is strongly influenced by sonication. The mechanism by which acoustic waves can be active at the molecular level is still a matter of speculation. The generally accepted "hot spot" theory,[9] whereby sonication produces "flash thermolysis-like" chemistry would favour a mechanism in which the initiation step could be the sonolysis of **1**.[10]

Under our conditions however, **1** is recovered quantitatively after 3h irradiation, which dismisses the direct initiation of **1** to **5**. The absence of this reaction also demonstrates that the initial electron transfer leading to **4** must take place between **1** and **2** with at least one of these reagents being in a different state from the fundamental one which yields **3**. As stated by Chanón, Eberson and Kornblum[11] the electron tranfer between a donor (D) and an acceptor (A) in the ground state is far too endergonic to take place spontaneously. One or both of these species or a charge tranfer complex (DA), have to be excited to a state more prone to react. The reaction can also be made easier in the presence of a mediator.[12] This we did observe when 4-nitrocumene was added to the reaction (Scheme 2).

The exact nature of these possible excited states is not yet known. Further studies are presently under investigation to determine this important fundamental aspect of sonochemistry.



Scheme 2

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References and Notes

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5. Standing waves are obtained for a distance from the tip of the horn to the bottom of the flask corresponding to a multiple of half a wavelength — in the present case *ca* 3.6 cm. This was determined using copper powder in ethanol at the same temperature as the experiments.
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