Effect of high pressure on Michael and Henry reactions between ketones and nitroalkanes

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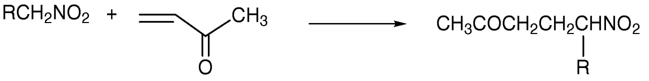
The kinetic pressure effect on some specific Michael and Henry reactions is investigated. The observed activation volumes of the Michael reaction between nitromethane and methyl vinyl ketone are largely dependent on the magnitude of the electrostriction effect, which is highest in the lanthanide-catalyzed reaction, still important in the aqueous reaction and lowest in the base-catalyzed version. In the latter case, the reverse reaction is insensitive to pressure. These results apply also to the Henry addition of nitroalkanes to ketones. The positive pressure effect can be used for the chemoselective synthesis of nitroalcohols from ketones.

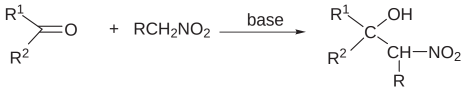
Together with the Diels–Alder cycloaddition, the Michael and aldol reactions are recognized as the most powerful and useful bond forming reactions in synthetic organic chemistry. In recent years, the use of nitroalkanes has been widely investigated as the compounds are versatile intermediates in C—C bond forming strategies, in addition to being readily available.[1] Nitroalkanes are particularly very appropriate reagents in Michael and aldol reactions, where they behave as α-hydrogen donors. Generally speaking, nitroalkanes react easily with typical Michael acceptors such as α,β-unsaturated aldehydes or ketones under base[2] or Lewis acid catalysis.[3] However, under such circumstances the reaction often suffers from a lack of selectivity since the reactive enolate may easily divert the reaction along other or further pathways. A notable improvement has been the discovery of water promotion on the addition of nitroalkanes to methyl vinyl ketone under neutral conditions[4] (Scheme 1).

The nitroaldol addition, also known as the Henry reaction, is a centennial reaction. Its usefulness has been highlighted mostly in the last decade as demonstrated by the abundant literature reviewed by Rosini.[5] In addition, the reaction has been found to be appropriate for the synthesis of optically active compounds.[6] The reaction is a classical C—C bond forming process requiring the use of a base, although to our knowledge there is no known example of a nitroaldol addition taking place under strictly neutral conditions. In a recent article, in analogy with the results obtained for a Michael reaction in aqueous solution,[4] water was also shown to improve the reaction: however a minimum amount of base was nevertheless required[7] (Scheme 2).

The reaction is usually facile when $R_1 = H$. However, as in Michael reactions, a number of secondary reactions can occur, depending on the nature of the base, temperature and concentration conditions.[8] When ketones are considered as substrates, the nitroaldol reaction becomes increasingly difficult, with yields of nitroalcohols reaching abysmal values, especially when R, R_1 and/or R_2 are bulky.



Scheme 1



Scheme 2

Some time ago, it was reported that the reactivity of nitroalkanes in Michael[9] and Henry[10] reactions could be enhanced by carrying out the additions under high pressure. The five aforementioned reports[9,10] were all short communications giving only fragmentary information. In this regard, we were moved to initiate a study on the quantitative pressure effect in nitro Michael and nitroaldol reactions in an attempt to locate the transition state and eventually to develop a chemoselective preparative method using high pressure.

Results

Effect of pressure on nitro Michael reactions

For our purpose, we chose the simple reaction involving nitromethane and methyl vinyl ketone (MVK), which may be considered as a prototypical Michael reaction. As expected, the addition did not occur in the absence of base. It proceeded in aqueous solution as described in the literature, however with lower rates than reported.[4] Some Michael reactions can also be achieved under lanthanide catalysis[11] and we have, therefore, investigated the pressure effect on the reaction between MVK and nitromethane effected in (*a*) tetrahydrofuran in the presence of tetrabutylammonium fluoride, (*b*) water under neutral conditions, and (*c*) chloroform in the presence of $Eu(fod)_3$. The observed kinetic results are listed in Table 1. Activation volumes $\Delta V^{\neq}$ were determined from the response to pressure of the observed rate constant (k_{obs}) in the pressure range 0.1–200 MPa according to the known relationship:

$$[\partial \text{ Ln } k_{obs}/\partial P]T = -\Delta V^{\neq}_{T}/RT$$

Under the conditions shown in Table 1, the aqueous and the lanthanide-catalyzed reactions were found to be non-reversible and to follow pure second-order kinetics. In the base-catalyzed process, even at the low concentration of the fluoride ion indicated in Table 1, the reversibility of the reaction was evident. The apparent second-order rate constant

Table 1 Effect of pressure on the Michael reaction between MVK and nitromethane

	Water	Chloroform	Tetrahydrofuran
T/°C	49.0	62.4	25.5
Catalyst	None	Eu(fod)$_3$ (2.5×10^{-2} M)	$Bu_4NF \cdot 3H_2O$ (10^{-3} M)
MVK/M	0.03	1.5	1
k_0 [a]/dm^3 mol^{-1} s^{-1}	6.85×10^{-5}	1.9×10^{-6}	2.9×10^{-5}
$\Delta V^{\neq}_{T}$/cm^3 mol^{-1}	−35.5	−55	−20.1
$\Delta V^{\neq}_{20}$ [b]/cm^3 mol^{-1}	−31.5	−46.5	−19.7

[a] Pseudo or effective second-order rate constant at atmospheric pressure (see text). [b] Calculated activation volume at 20.0 °C according to El'yanov's procedure.[12]

experimentally observed at the equilibrium was plotted against pressure to yield the pseudo $\Delta V^{\neq}$ value reported in Table 1.

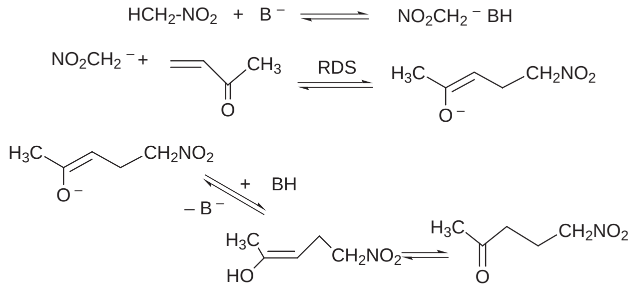
The diversity of experimental conditions prevents a precise comparison of rate constant values. At ambient temperature, only the base-catalyzed process is found to operate. A most interesting observation is the very variable pressure effect since the observed $\Delta V^{\neq}$ values range from −20 to *ca.* −50 cm^3 mol^{-1} (after homogenization to $T = 20$ °C[12]). In all cases pressure promotes the nitro Michael reaction.

The Michael reaction is a multistep process. According to the traditional Scheme, the base-catalyzed version involves the formation of the nitronate carbanion in the initial stage. The S_N2 reaction profile of the deprotonation of nitroalkanes has been described.[13] The second step is the rate-determining step, with nucleophilic attack on the electrophilic β-position of the ketone acceptor yielding the enolate, followed by rapid proton transfer (Scheme 3).

In considering the base-catalyzed reaction (case a), $\Delta V^{\neq}_{obs}$ is a composite quantity. The effect of pressure on the observed rate constant would be given by:[14]

$$RT(\partial \ln k_{obs}/\partial P) = -(\Delta V_1 + \Delta V^{\neq})$$

where ΔV_1 is the volume change in the first equilibrium step and $\Delta V^{\neq}$ the activation volume of the rate-determining step. ΔV_1 is expected to be zero as the first step involves breaking and formation of one bond with no change of ionic charges. The activation volume $\Delta V^{\neq}$ is a combination of $\Delta V^{\neq}_{s}$ (structural component) and $\Delta V^{\neq}_{e}$ (environmental component, mostly depending on charge generation or collapse). However, the process does not need extended pressure assistance since the fluoride ion in Bu_4NF is a relatively strong base. The overall value of $\Delta V^{\neq}$ would therefore mostly reflect $\Delta V^{\neq}_{s}$, namely the volume arising from the formation of the single C—C bond. The value found (around −20 cm^3 mol^{-1}) is close to the reaction volume, measured to be -20.8 ± 0.5 cm^3 mol^{-1} at 20 °C. As a logical conclusion, when the reactants enter the transition state, it appears that the C—C bond is largely complete, resulting in a product-like transition state. However, this approximation presents a major shortcoming in the sense that the observed activation volume is not a simple reflection of the forward reaction; it must also accommodate the reverse reaction. For this purpose, in the next phase we investigated the pressure effect on the reverse reaction and determined k values under pseudo-first-order conditions for two different concentrations of the fluoride anion (Table 2).



Scheme 3

The observed activation volume amounts to 0 ± 1 cm^3 mol^{-1} and does not depend on the base concentration. Hence, this retro-Michael reaction is practically insensitive to pressure, in apparent agreement with the principle of microreversibility. However, as in the case of the forward reaction, the observed $\Delta V^{\neq}$ is a composite quantity. In addition, the $\Delta V^{\neq}$ values for both bond-making and bond-breaking processes normally have to allow for some charge build-up, although very probably to a small extent (*vide supra*).

In order to check these values, we examined the parent base-catalyzed nitro Michael reaction between nitromethane and the hindered unsaturated ketone mesityl oxide (Scheme 4). A notable characteristic is that nucleophilic attack occurs on the most sterically congested carbon atom with, obviously, a considerable slowing of the rate.

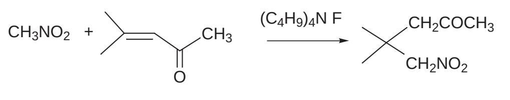
The pressure kinetics of the reaction were followed and the apparent activation volumes determined:[15] $\Delta V^{\neq}_{T} = -24 \pm 1$ cm^3 mol^{-1} whence $\Delta V^{\neq}_{20} = -21.1$ cm^3 mol^{-1} with a measured reaction volume $\Delta V_{20} = -21.7 \pm 0.5$ cm^3 mol^{-1}. Both Michael reactions investigated would apparently exhibit late transition states.[16,17] However, we are aware that this could be a weak argument to assess our mechanistic perception since the complete description of the volume profile *via* the activation volume is not established.

In neutral aqueous conditions (case b), the reaction was fully chemoselective as reported previously[4] (Table 1). One further aspect was its irreversibility and as such, the mechanistic Scheme 3 may be used. The slight acidity of nitromethane makes the nitronate anion a suitable base for nitro Michael reactions. However, the formation of the enolate must be

Table 2 Effect of pressure on the retro-Michael reaction of 1-nitro-4-pentanone[a]

Pressure/MPa	10^5k s^{-1} [b]	
1	4.71	1.63
50	4.73	—
100	4.65	1.60
200	4.75	1.58

[a] Solvent (THF), T (25.5 °C), nitro compound (0.4 M). [b] $[Bu_4NF \cdot 3H_2O] = 2.5 \times 10^{-2}$ M (left column) and 1.2×10^{-2} M (right column).



Scheme 4

assisted. As pressure is a powerful ionogenic method, electrostriction will be reflected in the value of the activation volume (-35.5 cm^3 mol^{-1}), meaning a stronger pressure-sensitive addition than the base-catalyzed reaction. However, the additional volume component cannot be fully ascribed to $\Delta V^{\neq}_{e}$, since complex effects intervene with consequences on the volume profile: hydrophobic effects (which are disfavored by pressure) and hydrogen bonding (which is promoted by pressure).[18] The pressure effect on aqueous organic reactions will be reported in due course.

The lanthanide-catalyzed Michael reaction (case c) is extraordinarily sensitive to pressure ($\Delta V^{\neq} = -55$ cm^3 mol^{-1}), comparable to the effect observed in the conjugate addition of amines to acrylic esters.[19] It is clear that in the present case, as most of the enolate is generated under pressure, there must be a major shrinkage of the reaction species along the reaction coordinate. In the process, the europium compound would have a dual character.[20] The oxophilicity of Eu^{3+} towards the carbonyl oxygen would increase the electrophilicity of the acceptor by coordinative activation. The ketone complexed by the lanthanide would subsequently be attacked by the nitronate according to Scheme 3. We suggest that the process is assisted by pressure in view of the strongly negative $\Delta V^{\neq}$ value, consistent with a large build-up of charge in the transition state. This property has been recently applied in the high-pressure Michael addition of β-ketoesters with various acceptors on silica gel supports.[21]

Interestingly, the $\Delta V^{\neq}$ values shown in Table 1 are in harmony with other activation parameters; whereas activation energy is little affected, the values of $\Delta S^{\neq}$ differ significantly (Table 3). In the lanthanide-catalyzed process the strongly negative value of $\Delta S^{\neq}$ can be ascribed to the formation of a dipolar zwitterionic transition state, the two charged centers requiring solvation with substantial entropy losses.[19]

Effect of pressure on nitroaldol reactions

Like the Michael addition, the nitroaldol reaction between a ketone and nitromethane occurs only in the presence of a base. Selecting cyclohexanone as the ketone, we first screened the best experimental conditions to carry out the reaction in a selective way: the temperature must be as low as possible (20–35 °C) in order to limit reversal to reactants, the concentration of $Bu_4NF \cdot 3H_2O$ should not exceed 3 mol% and the reactants should serve as the reaction medium. Unlike the nitro Michael addition, the nitroaldol reaction did not proceed either in aqueous solution (without the base)[7] or in the presence of a lanthanide catalyst in chloroform solution even under high pressure.

Table 3 Activation parameters for the addition of nitromethane to methyl vinyl ketone

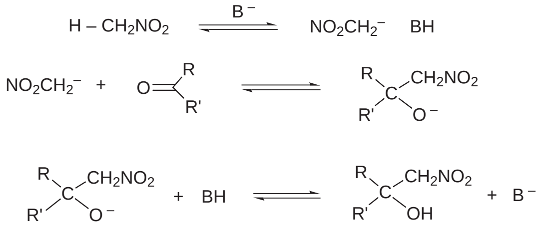
Medium	Catalyst	E/kJ mol^{-1}	$\Delta S^{\neq}$/J mol^{-1} K^{-1}
Water	None	49.7	-160.9
Chloroform	$Eu(fod)_3$	52.2	-219.5

The generally accepted mechanism for the base-catalyzed process resembles Scheme 3 (portrayed for the Michael reaction); it involves formation of the nitronate anion and subsequent nucleophilic attack followed by rapid protonation (Scheme 5). Depending on the conditions, other reaction pathways may occur, particularly base-catalyzed elimination to yield the nitroalkene, which can undergo a Michael addition involving a second molecule of nitromethane and polymerization (for further possibilities see ref. 5 and 8). Once the experimental conditions defined as above were optimized, we investigated the pressure kinetics of four Henry reactions (Table 4).

For the forward reaction the observed activation volume values range from -20.5 to -25.2 cm^3 mol^{-1}. They are close to the values of the reaction volume. The kinetics of the reverse Henry reaction involving nitromethylenecyclopentanol were found to be insensitive to pressure. These values are comparable to the $\Delta V^{\neq}$ values determined for the addition of nitromethane to methyl vinyl ketone and mesityl oxide. Hence, the nitroaldol reaction proceeds uneventfully in the same manner as the base-catalyzed nitro Michael reactions described in the first part of this paper, probably *via* a late transition state.

The observed $\Delta V^{\neq}$ values of the present nitroaldol reactions are indicative of a kinetic pressure effect, which is lower than in Diels–Alder reactions for which $\Delta V^{\neq}$ can take values as low as -40 cm^3 mol^{-1}.[22] Nevertheless, the calculated k_p : k_o ratios can be significant enough (Table 5) to make pressure activation an interesting synthetic strategy (Scheme 6 and Table 6).

In these nitroaldol reactions it was better to select the ketone as the reaction medium since its melting point is less sensitive to pressure as compared to nitroalkanes.[23] As an example, the yield of the adduct formed from the addition of excess nitromethane to 3-methyl-2-butanone dropped to 9%



Scheme 5

Table 5 Calculated $k_p : k_o$ values for $\Delta V^{\neq} = -20$ cm^3 mol^{-1} at 25.0 °C[a]

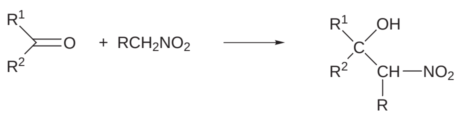
Pressure/MPa	$k_p : k_o$
100	2.1
300	6.6
500	16.4
750	35.2
1000	68

[a] k_p, k_o; rate constants at pressure P and atmospheric pressure, respectively.

Table 4 Apparent activation volumes of nitroaldol reactions involving ketones[a]

Ketone	Nitroalkane	T °C	$\Delta V^{\neq}_{T}$/cm^3 mol^{-1}	ΔV_T/cm^3 mol^{-1}
Cyclopentanone	Nitromethane	24.5	-20.5	-22.5
Acetone	Nitromethane	27.5	-22.0	-24.6
3-Pentanone	Nitromethane	32.7	-21.5	[b]
Acetone	Nitroethane	27.5	-25.2	[b]

[a] Base (0.03 mmol), ketone (1 mmol), nitroalkane (considered as solvent, 1 mL). [b] ΔV_T has not been determined.



Scheme 6

under 750 MPa whereas 60% of the corresponding nitroalcohol was obtained at the same pressure with an excess of ketone. Interestingly, the Henry reaction proceeds very cleanly at high pressure, probably as a result of the antagonistic pressure effect on dehydration of the nitroalcohol. Such elimination occurs readily under basic conditions to give nitroalkenes, which in turn polymerize.[24] For runs above 500 MPa, paper chromatography indicates in all cases formation of the nitroalcohol as the unique product. This selectivity is at variance with the reported Henry–Knoevenagel condensation between aromatic aldehydes and nitroalkanes to yield aromatic nitroalkenes even under pressure, as a result of electronic effects.[25]

We also tried to perform the Henry reaction in water under conditions nearly identical with those reported in ref. 7. The yield of adduct obtained from the addition of nitromethane to cyclopentanone after 24 h was 1.1% (to be compared to 11% under the conditions of Table 6). A more recent article suggested the use of tetramethylguanidine (TMG) as an appropriate base in Henry reactions involving aldehydes and alicyclic ketones.[26] We carried out some of the reactions listed in Table 6 by substituting TMG for the fluoride. The yields were slightly depressed at 0.1 MPa and the reaction exhibited lower selectivity due to the possibility of self-condensation of ketones, as also reported in ref. 26. However, the use of high pressure led to yields comparable or slightly higher than those obtained when using the fluoride.

Conclusion

The $\Delta V^{\neq}$ data for the nitro Michael reaction carried out in water or in the presence of a lanthanide catalyst give suggestive evidence for the dominance of ionic generation over covalent bond-making where the volume is concerned. The pressure accelerative effect can be viewed presumably as a result of late transition states. At variance, in both base-catalyzed nitro Michael and Henry reactions it is difficult to get a complete view of the reaction profile due to the reversibility of the different steps. The forward reactions show a comparable pressure effect in both reactions whereas the retro-Michael and the retro-Henry reactions do not respond to pressure, at least under the experimental conditions used.

Despite a lower kinetic effect than those reported for [4 + 2] cycloadditions, high pressure is a valuable tool for performing nitro Michael and Henry reactions as it improves not only yields but also selectivity.

Experimental

High pressure nitroaldol synthesis

In a typical synthetic run, 1,2,3-trimethoxybenzene (internal standard) and tetrabutylammonium fluoride are weighed and placed in a flexible PTFE tube (4 mL). Then the nitroalkane (6–7 mmol) is introduced *via* syringe and weighed. The tube is filled up with the appropriate ketone and placed into the thermoregulated vessel LV30/16 coupled to the hydraulic press U101 from Unipress (Warsaw). After pressurization to the desired pressure for 24 h, the mixture is collected. After washing with water, the organic fraction is collected and volatile compounds removed on a rotary evaporator. The residue is analyzed by NMR spectroscopy (Bruker AC 200) and the yield determined from the relative intensities of characteristic protons of the nitroaldol *versus* methoxy groups of the internal standard. The nitroalcohols obtained are pure enough to be easily characterized. As an example: 1-nitro-2,3-dimethyl-2-propanol: 4.37 (q, CH_2), 2.94 (br, s, OH),1.68 (m, CH), 1.09 (s, CH_3), 0.84 (d, CH_3).

The aqueous nitroaldol reaction between nitromethane and cyclopentanone was carried out according to ref. 7: nitromethane (3.7 mmol) was added to the ketone (3.4 mmol) in a 15 mL water solution of NaOH (0.375 mmol) in the presence of cetyltrimethylammonium bromide (0.5 mmol). After 24 h stirring, the mixture was worked up as described in ref. 7.

Kinetic experiments

For Michael reactions, a stock solution is prepared by weighing tetrabutylammonium fluoride, 1,2,3-trimethoxybenzene (standard) and nitromethane. This solution is kept at −5 °C. For a kinetic run, the unsaturated ketone is placed in a 1 mL PTFE tube and weighed. An adjusted volume of the stock solution (about 100 μl) is added and weighed. Finally, the tube is filled up with tetrahydrofuran before introduction in a specially built high-pressure vessel adapted to kinetic measurements (up to 300 MPa). After reaction the solution is washed twice with water and the organic layer collected by extraction with dichloromethane. The final residue is analyzed by high resolution ^1H NMR.

For nitroaldol experiments, the kinetic procedure is nearly identical except that one of the substrates serves as solvent.

The kinetics of the aqueous nitro Michael reaction are followed in large (15 mL) PTFE tubes. After reaction the organic layer is collected and analyzed either by NMR as above (1,2,3-trimethoxybenzene as standard) or by GLPC (mesitylene as internal standard) under chromatographic conditions (Girdel 300, PPE 7% on Chromosorb GAW DMCS-pyrex, 60–230 °C). In order to achieve homogeneous rate constants, the concentration of the reactants is kept low enough to ensure that no visual turbidity or separation occurs after mixing the substrates with water.

Table 6 Effect of pressure on the Henry addition of nitroalkanes to ketones[a]

				% Yield of nitroalcohol at P^b				
R	R_1	R_2	T/°C	0.1	300	500	750	950
H	CH_3	CH_3	33	18	63	100	—	—
H	CH_3	C_2H_5	25	9	—	—	100	—
H	CH_3	iC_3H_7	33	3	—	—	60	—
H	C_2H_5	C_2H_5	33	2	8	—	37	75
H	$-(CH_2)_4-$	$-(CH_2)_4-$	27	11	41	95	—	—
H	$-(CH_2)_5-$	$-(CH_2)_5-$	25	27	100	—	—	—
CH_3	CH_3	CH_3	27	14	43	—	—	—
CH_3	CH_3	C_2H_5	25	low	—	—	48	—
C_2H_5	CH_3	CH_3	25	4	14			
iso-C_3H_7	CH_3	CH_3	27	0	low			

[a] Nitroalkane (5–7 mmol), $Bu_4NF \cdot 3H_2O$ (0.08–0.1 mmol), solvent ketone: 4 cm^3), 24 h. [b] Based on ^1H NMR. Pressure is given in MPa.

The compounds necessary to run the retro-Michael and retro-Henry reactions are purified after synthesis by flash column chromatography.

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