

Liquid-phase oxidation of cyclohexene and of tetralin by N₂O in the presence of onium salts under mild experimental conditions

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Abstract

Cyclohexene and tetralin can be oxidized to a slight extent by N₂O in the presence of quaternary ammonium salt promoters under mild experimental conditions. In non-polar solutions, the higher yields of the oxidations of cyclohexene and tetralin are influenced by the donor–acceptor properties of the solvents. The changes in the IR spectrum of N₂O lend further support to the assumption that ion-pair interactions between the solvated oxidant and the onium salts result in an enhanced rate of O-transfer from the oxidant. Onium-decavanadate ion-pair complexes are more effective promoters than simple onium salts.

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1. Introduction

In the early 1950s, N₂O was applied for the oxidation of olefins [1], for the oxidative fission of double bonds [2] and for the oxidation of acetylenes [3]; rather vigorous experimental conditions were required: temperatures of 200–400 °C and pressures up to 2000 atm. More recently, it was recognized that N₂O can be activated by certain ruthenium complexes, among them porphyrin derivatives [4,5]. Attempts have subsequently been made to use N₂O as a liquid-phase oxidant in the absence of any catalyst. Panov et al. [6] reported that cyclohexene (Ch) can be oxidized by N₂O in the temperature range 150–250 °C at 53–120 atm, cyclohexanone being formed as main product with high selectivity.

N₂O is regarded as a rather unreactive gas. Its molecule is linear and non-symmetrical: the N–N and N–O distances are both short, at 112.6 and 118.6 pm, respectively, and calculations give the bond orders as N–N 2.73 and N–O 1.61. Its dipole moment is low, 0.166 D [7], suggesting that N₂O might be activated by

onium salts (generally denoted as Q⁺X[−]) via interactions due to the polarizing abilities of the ion-pairs. To check this assumption, the liquid-phase oxidations of Ch and tetralin (T) by N₂O were investigated in the presence of quaternary ammonium salts and onium-decavanadate ion-pair complexes as promoters under mild experimental conditions, both in the absence and in the presence of non-polar solvents.

2. Experimentals and methods

2.1. Reagents

The materials used and the methods applied for their purification are detailed elsewhere [8]. Phase-transfer catalysts (PTCs, Aldrich) were used without purification. Oxidant N₂O (Ph. EUR 4 grade) was supplied by Linde Co., Répcelak, Hungary.

It was recently reported [8] that O₂ is able to oxidize Ch and T in the presence of onium salt promoters. Accordingly, it was essential to check whether the anesthetic-grade oxidant N₂O contains O₂ or other oxidizing impurities. To this end, different methods were applied.

Gas chromatography (on a molecular sieve 5A column) revealed that the O₂ content was <0.03%. The presence of traces

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of O₂ in N₂O is an indication that not even traces of NO can be present, because NO reacts instantly with O₂.

Checks were also made on the presence of the less probable impurities of this grade of N₂O, the various compounds NO_x. For this, 40 cm³ 0.2 mol dm⁻³ NaOH solution was saturated by slowly bubbling through it about 60 dm³ N₂O finely dispersed with the aid of a sintered glass pipe. The solution was then neutralized with HCl and carefully evaporated down *in vacuo*. No NO₂⁻ or NO₃⁻ could be detected by spot tests [9] in the solid obtained.

It should be mentioned that the iodometric assay of O₂ by the method of Winkler [10], in which the injected N₂O sample is intensively stirred with an absorbent (a Mn(OH)₂ slurry), furnished considerably higher figures (in the interval 4–15%), depending on the length of the contact time. This observation suggests that not only O₂ impurity, but also N₂O itself, can be slowly reduced by Mn(OH)₂. This conclusion is supported by the fact that N₂ formation could be detected, to an extent increasing with time. Hence, this otherwise useful volumetric method cannot be applied for the determination of O₂ impurity in N₂O. However, there can be no doubt as to the correctness of the gas chromatographic results. It may safely be concluded that the oxidations of Ch and T, if they occur at all, should be overwhelmingly ascribed to N₂O, the contributions of O₂ and other oxidizing impurities in N₂O remaining well below 1%.

2.2. Onium-decavanadate ion-pair promoters

Appropriate aqueous NaVO₃ solutions were adjusted to pH 4.5 with HCl, when H₂V₁₀O₂₈⁴⁻ is formed [11,12]. These solutions were extracted with the PTCs Hex₄NCl and Me(Oct)₃NCl (the latter known as Aliquat 336; ALCl) (both insoluble in water) dissolved in chlorobenzene. The two phases were mixed in equal volumes and stirred efficiently (at 3000 rpm) for 30 min. After separation of the phases, the organic phase was filtered on a Whatman 1PS silicone-treated phase-separator and stored at room temperature in the dark. The efficiency of extraction was checked by estimating the vanadium(V) content [13] in the separated aqueous phase. For type A onium-decavanadate promoters, the quantity of PTC applied was just sufficient to neutralize the negative charges on H₂V₁₀O₂₈⁴⁻, i.e. the concentration ratio of onium salts to vanadium(V) was 4:10; for type B onium-decavanadate promoters, the PTC was used in a 2.5-fold excess, the concentration ratio here therefore being 10:10.

2.3. Oxidation of hydrocarbons

Samples of 8.00 cm³ Ch and/or T (without solvent) or 8.00 cm³ of their solutions in non-polar solvents with different donor–acceptor properties [14] were introduced into glass reactor (fitted with a reflux condenser and cooled with water at room temperature). To remove the atmospheric O₂, N₂ (sometimes with Ar) at room temperature was bubbled through the samples and the whole system for at least 5 min and intensive magnetic stirring was started. Next, the N₂ (Ar) atmosphere above the

reaction solution was quantitatively replaced by N₂O (the total volume of gas is about 100 cm³). Thereafter, the heating-jacket of the reactor was connected to a thermostat preheated up to 70 °C. After a 5-min warming-up period, the gas burette (also fitted with a thermostating jacket) filled with N₂O was switched on, and recording of the uptake of the oxidant in the dark was simultaneously started. During the runs the pressure of N₂O was always regulated at atmospheric level. After a conversion time of 120 min, the oxidate was flushed with N₂, cooled down quickly to room temperature and stored in a refrigerator at about 5 °C for subsequent gas chromatography and NMR investigations.

A Metrohm E 415 Multi-Dosimat was used as gas-measuring device. It was slightly modified, making possible measurements of both gas uptake and/or gas evolution (release), and connected to the reactor via a switching manometer (filled with 10% H₂SO₄). The latter helped to maintain the inside pressure automatically at atmospheric level. The 20 cm³ syringe gas burette was connected by a three-way tap to the reactor and to a poly bag for refilling the N₂O oxidant.

2.4. IR investigations

It was intended to collect physical evidence to support the kinetic observations on the activation of N₂O by onium salts. To this end, the solvents were purged with N₂ for 5 min to remove traces of O₂. After this, the N₂ atmosphere was fully replaced by N₂O, the gas burette was connected, the oxidant was allowed to dissolve at atmospheric pressure under intensive stirring for 5–10 h, and the gas uptake was noted.

The N₂O stock solutions so obtained could be stored without notable change under a protecting N₂O blanket (at atmospheric pressure) in a closed vessel for at least 1–2 days. However, the N₂O concentration dropped immediately when the vessel was opened. To avoid N₂O loss when these solutions were diluted or mixed with onium salt solutions and also when the IR cell was filled, the stock solution in the reactor was passed via a syphon fitted with a three-way tap either to the IR cell, or to a 4 cm³ mixing syringe. This latter initially contained 2.00 cm³ solvent or onium salt solution, to which 2.00 cm³ N₂O stock solution was added by the Dosimat at atmospheric pressure. After thorough mixing, the IR cell was filled from the mixing syringe.

The concentrations of the N₂O stock solutions were calculated from the N₂O uptake values; and estimated by gas chromatography (on a Molesieve 5A capillary column, 30 m, 0.32 mm).

The other details relating to the analysis of the oxidation reaction mixtures are described elsewhere [11,12]. Carlo Erba Fractovap 2400 V and a 6890 N Agilent gas chromatograph equipped with an HP-5 capillary column (30 m × 0.25 mm, 0.25 μm) and a 5973 MS detector were applied; and NMR spectra were recorded with a Bruker Avance DRX 500 NMR spectrometer. IR spectra were recorded with a Bio-Rad-Digilab FTS-65/896 instrument equipped with a DTGS detector. The resolution was 2 cm⁻¹ and 128 scans were collected for a spectrum. Spectra were evaluated with the WIN-IR software package.

3. Results and discussion

Schwab and Berninger [15] reported that N_2O dissolves to a considerable extent in water, but rather slowly. Similar behaviour has been observed in non-polar solvents. It has been found [16] that N_2O is fairly well soluble in chlorobenzene: the Ostwald solubility at 25 °C is 3.174 cm³ N_2O per cm³ solvent. We observed a higher solubility than this, and we were not able to reach saturation during 5–30 h at room temperature (22–24 °C) and atmospheric pressure. The fact that the saturation could not be attained in the solvents used may suggest the occurrence of aggregation with monomers, dimers, and even higher associated clusters in equilibrium. In this respect, it is instructive to consult a recent theoretical publication on the possibility of formation of N_2O clusters ([17] and the related references therein).

The absorption of N_2O in these non-polar solvents started at a moderate rate: 0.10–0.14 cm³ min⁻¹ (at 70 °C and atmospheric pressure). The rate then soon dropped off and after 8–10 min the rate remained constant at a lower level, 0.02–0.07 cm³ min⁻¹, for at least 5–30 h. The rates of N_2O uptake (in the later constant section) followed the sequence: diethyl carbonate \approx acetonitrile > chlorobenzene > Ch > T > carbon tetrachloride. It should be mentioned that the rate of dissolution of N_2O was slightly altered by the change in surface tension of the given solutions when onium salts were also present.

It should be emphasized repeatedly that N_2O solutions can be stored only under a protecting N_2O blanket at atmospheric pressure. This is only one of the reasons why the oxidation of hydrocarbons could not be investigated by measuring the change in concentration of the N_2O in the reaction mixture in time. Moreover, N_2 is known to be evolved simultaneously with O-atom transfer from N_2O in the oxidations. In consequence of this, the progress of the oxidations of hydrocarbons by N_2O cannot be followed simply by recording the N_2O uptake in time, which is a convenient procedure in oxidation by O_2 [8]. This is the reason why we do not report N_2O uptake values. Instead, the concentrations of the oxidation products of the hydrocarbons were determined after conversion for 120 min. These results are presented in Table 1.

An attempt was made to determine the total amount of N_2 formed (both the amount dissolved in the reaction mixture and the larger amount that escaped into the gas phase). Unfortunately, in consequence of the considerable dilution of the N_2 in the gas phase, the total N_2 levels obtained were not sufficiently accurate to serve as controls of the data obtained by analysis of the oxidation products.

During the oxidation of Ch by N_2O , in the absent of any solvent, very little 2-cyclohexen-1-ol (Ch-ol) was formed; the amount increased when onium salts were applied. In contrast, in non-polar solvents Ch was oxidized in considerably greater extent; please observe, that only a quarter quantity of Ch was applied in these cases. In chlorobenzene (DN: <2) solution, cyclohexene oxide (Ch-O) is formed besides Ch-ol. These products are increased when onium salt were applied. However, in solvents of higher DN (acetonitrile: DN 14.1, diethyl carbonate: DN \geq 16), the oxidation of Ch is somewhat suppressed. In the acceptor solvent carbon tetrachloride (AN: 8.6), Ch is oxidized

to a similar extent. It should be stressed that other oxidation products of Ch could not be detected at all by either traditional or MS gas chromatography under the mild experimental conditions used. These products were confirmed by NMR measurements.

It should be borne in mind, however, that cyclohexanone was not formed during the oxidation of Ch. No traces of cyclohexanone could be detected either by MS gas chromatography or by NMR under the experimental conditions applied here. On the other hand, it should be remembered that cyclohexanone was the main product in the experiments of Panov et al. [6]. It seems probable that the isomerization of Ch-O into cyclohexanone may occur under such more vigorous experimental conditions (150–280 °C and 53–120 atm). This is likewise indicated by the observations of Flowers et al. [18], who found that 1,2-epoxycyclohexane decomposed in the gas phase in the temperature range of 680–740 K, at pressures between 1.6 and 6 Torr. The isomerization of Ch-O to cyclohexanone and Ch-ol occurred by first-order, homogeneous, non-radical processes, and accounted for ca. 97% of the primary products.

It may be concluded that in the presence of onium salts Ch is mainly oxidized by N_2O to Ch-ol by insertion of O-atom of the oxidant into the C–H bond of the π -weakened neighbouring CH_2 group, and less Ch-O is formed.

The oxidation of T could not be achieved in the absence of onium salts. In their presence, a little 3,4-dihydro-1(2H)-naphthalenone (α -tetralone, T-one) and much more 1,2,3,4-tetrahydro-1-naphthol (α -tetralol, T-ol) were formed. These results indicate that T is attacked by the oxidant at its 1 (or 4) CH_2 group (these H-atoms being activated by the adjoining benzene ring) by insertion of the O-atom; some oxidative dehydrogenation is also occurred and a little T-one was formed. It was also checked that a commercial T-ol preparation can be slightly oxidized by N_2O in the presence of onium salt promoters under identical experimental conditions.

In a chlorobenzene solution of T, T-one was the only product of oxidation. In acetonitrile and diethyl carbonate solutions, however, no oxidation of T was detected at all. The results obtained concerning the oxidation of T, and the lower yields observed for the somewhat more easily oxidizable Ch, allow the conclusion that the activation of N_2O by the onium salts is reduced or suppressed in solvents of higher DN number. It was found that only T-ol is formed in the acceptor solvent carbon tetrachloride with higher yield than in the slightly donor chlorobenzene solution.

It should be emphasized that neither in the absence nor in the presence of non-polar solvents were hydroperoxides of Ch and T ever obtained during oxidations with N_2O . This can be regarded as convincing evidence of the activation with the onium salts that facilitates direct O-atom transfer from the oxidant instead of promoting the decomposition of N_2O into O_2 and N_2 , which could also cause oxidation, but secondarily. In the latter case, however, hydroperoxides must be formed.

Onium-decavanadate ion-pair complexes proved to be better promoters than the simple onium salts for the oxidation of both hydrocarbons. The activities of the onium-decavanadate ion-pairs were found to depend on the quantities of onium salts used for extraction. Type A onium-decavanadate promoters were

Table 1
Products of the oxidations of hydrocarbons by N₂O (in mmol)

Solvent	Hydrocarbon	Promoter	Δ[Ch-O]	Δ[Ch-ol]	Δ[T-one]	Δ[T-ol]
None	Ch	None	0.000	0.020	–	–
	Ch	Hex ₄ NCl	0.000	0.095	–	–
	Ch	ALCl	0.000	0.037	–	–
	T	None	–	–	0.000	0.000
	T	Hex ₄ NCl	–	–	0.443	2.059
	T	Hex ₄ NI	–	–	0.190	1.215
	T	ALCl	–	–	0.412	1.041
Chlorobenzene	Ch	None	0.053	0.068	–	–
	Ch	Hex ₄ NCl	0.084	0.130	–	–
	Ch	ALCl	0.064	0.410	–	–
	Ch	Hex ₄ N-V(V) A	0.000	1.037	–	–
	Ch	Hex ₄ N-V(V) B	0.000	0.538	–	–
	Ch	AL-V(V) A	0.000	0.718	–	–
	Ch	AL-V(V) B	0.000	0.000	–	–
	T	None	–	–	0.000	0.000
	T	Hex ₄ NCl	–	–	0.821	0.000
	T	ALCl	–	–	0.499	0.000
	T	Hex ₄ N-V(V) A	–	–	2.483	0.000
	T	Hex ₄ N-V(V) B	–	–	1.795	0.000
	T	AL-V(V) A	–	–	1.767	0.000
	T	AL-V(V) B	–	–	0.000	0.000
Acetonitrile	Ch	None	0.000	0.020	–	–
	Ch	Hex ₄ NCl	0.034	0.046	–	–
	Ch	ALCl	0.069	0.065	–	–
	T	None	–	–	0.000	0.000
	T	Hex ₄ NCl	–	–	0.000	0.000
	T	ALCl	–	–	0.000	0.000
Diethyl carbonate	Ch	None	0.000	0.022	–	–
	Ch	Hex ₄ NCl	0.060	0.118	–	–
	Ch	ALCl	0.064	0.056	–	–
	T	None	–	–	0.000	0.000
	T	Hex ₄ NCl	–	–	0.000	0.000
	T	ALCl	–	–	0.000	0.000
Carbon tetrachloride	Ch	None	0.000	0.020	–	–
	Ch	Hex ₄ NCl	0.019	0.302	–	–
	Ch	ALCl	0.009	0.164	–	–
	T	None	–	–	0.000	0.000
	T	Hex ₄ NCl	–	–	0.000	2.585
	T	ALCl	–	–	0.000	1.076

Conditions. In the absence of solvents, the quantities of Ch and T, respectively, are 79.976 and 58.876 mmol. In the presence of solvents, the corresponding concentrations are 19.744 and 22.078 mmol, respectively. In each catalysed run (with onium salts and onium-decavanadate ion-pair complexes), 0.024 mmol (=0.003 mol dm⁻³) onium promoter ions were used.

more active than those of type B. In the latter case, excess onium salt was used to extract the decavanadate oligomer, whereby the activity of such ion-pair complexes was reduced, probably because of the presence of an excess of onium salts. Similar behaviour was earlier observed in the oxidations of these hydrocarbons by O₂ [12].

In the presence of decavanadate ion-pair complexes, Ch-O was not formed during the oxidation of Ch. In the oxidation of T, only T-one was obtained. It was observed in the oxidation of T that the initially faint-yellow solution turned dark greenish-brown, which is an indication of the partial reduction of vanadium(V). When this darker solution was flushed with N₂ immediately after completion of the oxidation, the dark colour remained permanently; if flushing was not performed, then, after a prolonged period of standing, even in the cold, the yellow

colour returned because of the reoxidation of vanadium by the N₂O remaining in the solution. The fact that partial reduction of the vanadium(V) was observed draws attention to the complex manner in which decavanadate anions function. Like other ion-pair anions, they regulate the partial positive charge of the quaternary atom via their polarizability [8,12] and they additionally act as a weak redox catalyst. Further experiments are called for to shed light on the latter role.

3.1. IR investigations

The fundamental IR vibrations of N₂O dissolved in non-polar solvents differ only slightly from those in the gas phase (Table 2). The interactions between N₂O and the solvent molecules are rather weak: merely small frequency shifts were observed. These

Table 2
Wavenumbers and absorption ratios of fundamental peaks of N₂O

	ν_3 : N–N-stretching \leftarrow N–N \rightarrow – \leftarrow O	ν_1 : N–O stretching \leftarrow N– \leftarrow N–O \rightarrow (frequency/cm ⁻¹)	ν_2 : Deformation \uparrow $\text{N}-\text{N}-\text{O}$ \downarrow \downarrow	Ratio of peak areas	
				1	2
Gas phase	2223.7 [21]	1284.9 [21]	588.8 [21]	6.31 [17]	49.20 [17]
Chlorobenzene	2218	1281	583	8.41	36.89
Acetonitrile	d. (2214)	1284	586	u.	13.01
	2228 [21]	1285 [21]	585.5 [21]	–	–
Diethyl carbonate	2224	n.d.	585	u.	40.00
Carbon tetrachloride	2218	1281	586	6.00	33.09
	2216 [21]	1281.3 [21]	586 [21]	–	–

Absorption ratios: 1: A_{ν_3}/A_{ν_1} , 2: A_{ν_3}/A_{ν_2} . d.: disturbed by strong self-absorption of the solvent; n.d.: not detected; u.: uncountable.

weak interactions may be one of the reasons for the sluggish dissolution of N₂O in non-polar solvents. In the interest of reducing possible errors arising from the preparation of the samples and the estimation of N₂O, the use of peak area ratios is preferred for the evaluation of promoter interactions. The results were as follows.

In chlorobenzene solution, all three fundamental peaks of N₂O can be observed. However, the regions of the N–O-stretching and deformation peaks are rather disturbed, and accordingly the areas of these bands cannot be given with sufficient accuracy. In the presence of higher onium salt concentrations, the ν_1 vibration band was broadened and lost its characteristic feature. Hence, the increase in peak ratio 1 cannot be given. The less informative ratio 2 is higher than the value obtained in the absence of onium salts. On this basis, the ion-pair interaction in this medium seems to be established.

Acetonitrile is not an appropriate solvent for an IR investigation of the N₂O solution. The strong self-absorption of the solvent, close to the N–N-stretching peak of the oxidant, does not allow the determination of peak areas. For this reason, the influence of the onium salts was not examined.

In diethyl carbonate, the ν_3 and ν_2 bands appeared, whereas the ν_1 band could not be seen because of the strong self-absorption of the solvent. Consequently, peak ratio 1 cannot be given at all, and the increased value of ratio 2 is not an absolutely conclusive indication of the interaction. In the course of the oxidation experiments, it was found that only the more readily oxidizable Ch could be oxidized slightly; T was not attacked at all. This was interpreted in that N₂O can at best be activated only slightly by onium salts in this electron-rich solvent (high DN).

The most reliable support for the occurrence of the ion-pair interaction of N₂O with onium salts is furnished by carbon tetrachloride as acceptor solvent. Here, all three fundamental peaks of N₂O were observed without any interference. In the absence of onium salts, the absorption ratios 1 and 2 are close to the values obtained in the gas phase, but in the presence of onium salts both peak ratios are altered. While the ν_3 peak was hardly changed, the ν_1 and ν_2 peaks decreased considerably in response to the presence of the onium salts; consequently, both ratios 1 and 2 are increased in this electron-withdrawing solvent.

When carbon tetrachloride was used, it was observed that both the rates of the oxidations of hydrocarbons by N₂O and the dissolution of the oxidant varied similarly in the presence of traces of water. In thoroughly dried solvent (with zeolite A) only the very slow dissolution of N₂O occurred and very minute extent of oxidation of the hydrocarbons were found. It should be borne in mind that catalysis and inhibition by water were observed during the liquid-phase oxidation of various hydrocarbons by O₂ [19]. In dried solutions, no oxidation by O₂ was observed during 120 min, while on the addition of traces of water the O₂ uptake soon started, and it increased up to a maximum as the concentration of water was elevated. The oxidation subsequently slowed down and practically stopped when water appeared as a separate phase. Such a water effect seems to be general and it is quite probable that water contributes to the change in the IR absorption of N₂O, too (the last three entries in Table 3 may be compared with the data on the undried samples). It must be emphasized, however, that the onium salts used are rather hygroscopic, and consequently the influence of the onium salts could not be investigated in an entirely water-free medium. IR investigations are currently in progress with a view to elucidating the role of water.

It is worthy of mention that the decomposition of the N₂O stock solution was also investigated in the presence of higher onium salt concentrations ($\geq 0.1 \text{ mol dm}^{-3}$) at room temperature during 2 days, but no formation of O₂ and N₂ could be detected by MS gas chromatography. This may be due to the proneness of these onium salts to undergo association. The promoted oxidation of Ch and T by O₂ proceeds according to a maximum curve (with maximum rate at about 0.02 mol dm^{-3}) which, after a limiting section, dropped rather abruptly to a low value near 0.1 mol dm^{-3} onium salt [20]. This was the reason why the oxidations of Ch and T by N₂O were not investigated at higher onium salt concentration.

To summarize the present results it may be stated that, additionally to the kinetic observations, the IR spectral changes furnished physical evidence and lent further credence to the working hypothesis that ion-pair interactions exist between the N–O moiety of the oxidant molecules and the cations of the onium salts. This results in the weakening of N–O bond and the slow oxidation of Ch and T under mild experimental conditions.

Table 3
IR absorption of N₂O solutions in the absence and in the presence of onium salt promoters

N ₂ O solution	Hex ₄ NCl (mol dm ⁻³)	ALCl (mol dm ⁻³)	Peak areas of vibrations			Ratio of peak areas	
			ν_3	ν_1	ν_2	1	2
Chlorobenzene	None	None	4.89	0.58	0.13	8.43	37.08
	0.153	None	0.79	n. d.	n. d.	u.	u.
	None	0.153	2.73	n. d.	n. d.	u.	u.
	None	None	13.75	1.65	0.36	8.33	38.19
	0.153	None	13.79	n. d.	0.32	u.	43.09
	None	0.153	11.73	n. d.	0.24	u.	48.87
	None	None	13.20	1.38	0.33	9.56	40.00
	0.153	None	13.59	n.d.	0.29	u.	46.57
Acetonitrile	None	None	11.48	n.d.	0.22	u.	50.59
	None	None	n.d.	0.78	0.12	u.	u.
Diethyl carbonate	None	None	2.43	utr.	0.05	u.	48.60
	0.152	None	2.32	utr.	0.04	u.	58.00
	None	0.152	2.43	utr.	0.04	u.	60.75
	None	None	7.85	utr.	0.16	u.	49.06
	0.060	None	5.68	utr.	0.13	u.	43.69
	None	0.061	1.24	utr.	0.03	u.	41.33
Carbon tetrachloride	None	None	25.41	4.27	0.63	5.95	40.33
	None	None	12.97	1.76	0.32	7.37	40.53
	None	None	12.91	1.83	0.31	7.05	41.64
	None	None	5.31	0.94	0.13	5.65	40.84
	0.155	None	5.29	0.26	0.11	20.34	48.09
	None	0.143	3.06	0.16	0.06	19.12	51.00
	None	None	6.97	1.23	0.17	5.66	41.00
	0.197	None	1.50	0.10	0.03	15.00	50.00
	None	0.0214	0.96	0.04	0.02	24.00	48.00
Carbon tetrachloride dried	None	None	6.74	1.08	0.16	6.25	41.57
	0.032	None	4.00	0.75	0.15	5.33	35.37
	None	0.031	5.07	1.12	0.14	4.54	35.47

Conditions. In each experiment the solvent or the corresponding onium salt solution was mixed with the N₂O stock solution in 1:1 ratio. utr.: untransparent; n.d.: not determined (extremely involved); u.: uncountable. Absorption ratios: 1: A_{ν_3}/A_{ν_1} , 2: A_{ν_3}/A_{ν_2} .

4. Conclusions

In liquid-phase oxidations, the considerable inertness of N₂O is attributed mostly to the multiply bonded O-atom rather than to the sluggish dissolution of the oxidant in the non-polar solvents. The kinetic results and IR observations prove the occurrence of direct O-atom transfer from N₂O to the hydrocarbon molecules, the oxidant being activated by the onium salts due to ion-pair interactions.

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