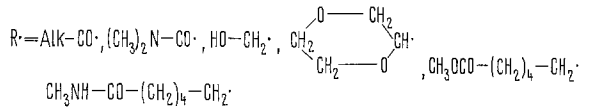
Because of the well-known influence of the polar characteristics of free radicals on their reactivity, it might be expected that a more enhanced reactivity would occur of nucleophilic radicals on the carbon atom of the nitrile oxide which possess a clear electrophilic character. It is known that the electrophilic or nucleophilic character of a free radical can be correlated with the oxido-reductive potentials of the equilibria:

$$R\cdot + e \rightleftharpoons R^-$$

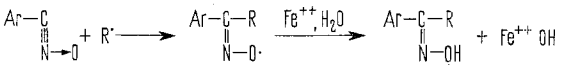
$$R\cdot - e \rightleftharpoons R^+$$

In a preliminary work[110] we allowed to react with aromatic nitrile oxides the following radicals of proved nucleophilic character:



generated in the presence of the nitrile oxide by suitable redox systems from aldehydes, dimethylformamide, methanol, dioxan, cyclohexanone etc.

In all the cases experimented reaction did occur according to the general scheme:



The products thus obtained are the oximes of α-diketones, α-ketols, α-ketoacids dimethylamides, aryldioxanylketones, ω-ketoesters and methylamides.

In its final result this reaction would consist in the 1,3-addition to nitrile oxides of aldehydes, formylamines, alcohols, ethers, esters and amides of monocarboxylic acids, and has therefore interest also for its possible synthetic applications.

Riassunto. Dopo una breve introduzione storica, viene dato un quadro delle attuali conoscenze sulla chimica degli ossidi di nitrili con particolare riguardo ai suoi più recenti sviluppi. L'applicazione di metodi già noti e l'introduzione di nuovi metodi di preparazione hanno portato alla cinquantina il numero dei nitrilossidi isolati, oltre a quelli numerosi preparati in situ e utilizzati in reazioni di addizione senza isolarli. Vengono esaminate le reazioni di dimerizzazione e polimerizzazione, le numerose reazioni di addizione nucleofila che mettono in evidenza lo spiccato carattere elettrofilo dei nitrilossidi e, in particolare le addizioni sopra i legami etilenici e acetilenici che portano a isossazoline e isossazoli. Nuove acquisizioni sperimentali, come l'isolamento in rese sostanziali e talvolta preponderanti di ossime acetileniche accanto agli isossazoli, rimettono sul tappeto la questione della via battuta da quest'ultima reazione, suggerendo come possibile alternativa al meccanismo generalmente ammesso di cicloaddizione 1,3-dipolare concertata quello che passa attraverso uno «zwitterione» intermedio, dal quale tanto l'isossazolo che l'ossima possono prendere origine. Viene illustrato l'effetto catalitico del BF_3 su alcune reazioni di addizione dei nitrilossidi, che consente l'ampliamento del campo di applicazione di queste reazioni. Vengono infine riportati i primi risultati dello studio della reattività dei nitrilossidi verso i radicali liberi al carbonio, studio che appare suscettibile di interessanti sviluppi.

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SPECIALIA

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A Correlation of the Ionization Energies of Water and Ethers with the Polar and Inductive Substituent Constants

A wide variety of structure and reactivity data have successfully been correlated by the Hammett and Taft equations[1].

The ionization potentials of alkyl free radicals, $R\cdot$, have been correlated[2] with Taft's polar substituent constants, σ^*.

We now demonstrate that the ionization energies of ethers, R_2O, are also a linear function of both σ^* and σ_I.

The gas-phase expulsion of an electron from the nonbonding lone pair on the oxygen atom of an ether molecule is in accord with the equation:

$$R\text{-}\ddot{O}\text{-}R \xrightarrow{E_I} R\text{-}\dot{\overset{+}{O}}\text{-}R + \bar{e}.$$

and the ionization potential, E_I, of course, corresponds approximately to the energy of the highest occupied

Table I

R-group	E_I[7]	σ^*	σ_I
H-	12.59	+0.49	0
Me-	10.00	0	—0.046
Et-	9.53	—0.10	—0.055
n-Pr-	9.27	—0.12	—0.058
i-Pr-	9.20	—0.19	—0.064
t-Bu-	–[a]	—0.30	—0.074

[a] Experimental value not available.

Table II

Ether	E_I (ev.) (Exp't.)[7]	E_I (ev.) (Eq. 1a)	E_I (ev.) (Eq. 2)
H_2O	12.59	12.53	12.59
Me_2O	10.00	10.00	10.01
Et_2O	9.53	9.49	9.51
nPr_2O	9.27	9.38	9.34
$i\text{-}Pr_2O$	9.20	9.02	9.01
$t\text{-}B\mu_2O$	–[a]	8.45	8.44
t-BuOMe	–[a]	9.23	9.22

[a] Experimental value not available.

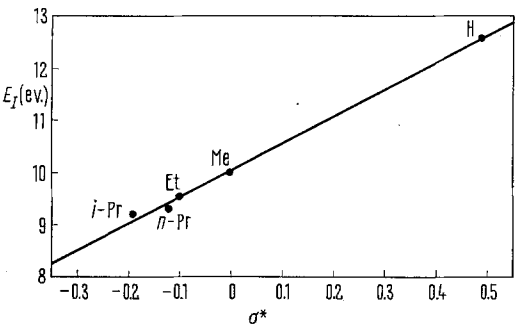

Fig. 1. A plot of the ionization energies, E_I, of the ethers versus the polar substituent constants, σ^*, of the corresponding *R*-groups.

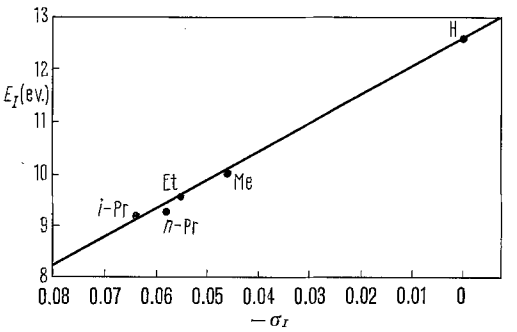

Fig. 2. A plot of the ionization energies, E_I, of the ethers versus the inductive substituent constants, σ_I, of the corresponding *R*-groups.

molecular orbital[3,4]. The entire chemistry of ethers, in fact, is dominated by the behavior of the $2p$ oxygen lone pair electrons[5]. Electron-releasing alkyl groups bonded to an *O*-atom of an ether molecule should obviously facilitate the electron removal, and thereby lower the E_I; and the presence of electron-withdrawing *R*-groups should likewise cause an increase in the requisite ionization energy[6]. It is interesting that we are able to include water as the simplest ether in the series.

Table I presents the σ^* and σ_I values Ref. Nos. together with the ionization potentials (ev.) for various aliphatic ethers[7] and water.

An excellent correlation is shown in Figure 1 where the E_I values are plotted *vs.* σ^*. The equation for the regression line is given by the following:

$$E_{R_2O} = E_{Me_2O} + a^* \sigma^*. \quad (1)$$

The slope, a^*, is found to be 5.15 and therefore we have:

$$E_{R_2O} = 10.00 + 5.15\,\sigma^* = 10.00 + 2.57\,\Sigma\sigma^*. \quad (1a)$$

Using, instead, the inductive substituent constants, σ_I, of TAFT and LEWIS[8], one obtains the correlation shown in Figure 2, from which we find

$$E_{R_2O} = E_{H_2O} + a_I\,\sigma_I = 12.59 + 56.0\,\sigma_I = 12.59 + 28.0\,\Sigma\sigma_I. \quad (2)$$

This indicates that the effect of the alkyl substituents on the *O*-atom is primarily an inductive one.

In Table II we show a comparison between the experimental ionization energies and those calculated using equations (1a) and (2).

Résumé. On démontre que les énergies d'ionisation des ethers, R_2O, sont une fonction linéaire des constantes substituentes polaires et inductives. Les groupes alkyls qui donnent des électrons abaissent l'énergie d'ionisation du «lone-pair» de l'atome d'oxygène. L'eau est inclue dans la corrélation de même que l'ether le plus simple. On trouve qu'avec bonne approximation $E_I = 10{,}00 + 2{,}57\,\Sigma\sigma^*$ ou $E_I = 12{,}59 + 28{,}0\,\Sigma\sigma_I$.

BARBARA W. LEVITT and L. S. LEVITT

Chemistry Department, The University of Texas at El Paso, El Paso (Texas 79999, USA), 5 June 1970.

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