Radiation Induced Transformations of Benzaldehydes Carrying Formyl-, Nitro- or Nitroso-substituents in the *ortho* Position

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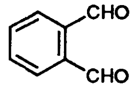
Transformations induced by X-irradiation of *o*-phthalaldehyde (**1**), *o*-nitrobenzaldehyde (**2**), and *o*-nitrosobenzaldehyde (**3**) isolated in argon matrices are described. It is shown that the formyl hydrogens in **1**, **2** and **3** spontaneously migrate to the respective *o*-substituents upon ionization. The resulting radical cations are characterized mainly by the ketene and OH stretching bands in their IR spectra.

In all cases, X-irradiation led also to the formation of substantial amounts of the neutral tautomers as well as other products in the case of **2** and **3**. These are thought to arise by way of the corresponding radical cations which are reneutralized by scavenging some of the electrons ejected from the matrix material upon X-irradiation.

Photochemical transformations of various *ortho*-alkyl substituted phenyl ketones and aldehydes have been the subject of numerous studies and the mechanism of the so-called photoenolization of these compounds is now well established.[1] More recently, radiolytic transformations of *o*-methyl substituted aromatic ketones and aldehydes have received attention, and it has been shown that upon ionization such compounds undergo spontaneous hydrogen transfer to form the radical cations of the corresponding enols.[2]

Few aromatic carbonyl compounds carrying *o*-substituents other than alkyl groups have been studied until now. Such sytems include *o*-phthalaldehyde (**1**),[3] *o*-nitrobenzaldehyde (**2**)[4] and *o*-nitrosobenzaldehyde (**3**)[5] whose photochemistry has been studied in some detail. In view of the interesting results we have recently obtained with the *o*-methyl substituted aromatic aldehydes and ketones[2] we decided to investigate the radiation induced transformations of **1**–**3** in argon matrices.

Matrix isolation spectroscopy in the UV–VIS[6] and more recently, in the IR range, where the high spectral resolution may offer a wealth of information,[2-7] has permitted the observation and characterization of numerous highly reactive radical cations which can often not be studied under ambient conditions. In the case of photoenols and their radical cations the characteristic UV–VIS spectra of the *o*-quinoid π-systems on the one hand and the intense ketene and OH stretching frequencies on the other hand served to identify the products of photolysis and/or radiolysis. This paper presents the results of a study where we apply the same techniques to compounds **1**–**3**.



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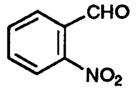

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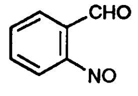

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Experimental

Materials.—*o*-Phthalaldehyde (Fluka) and *o*-nitrobenzaldehyde (Fluka) were used without further purification. *o*-Nitrosobenzaldehyde was prepared according to the procedure described by Bamberger[8] and the purified final product was characterized by UV–VIS and IR-spectroscopy.

Techniques.—The method of preparing radical cations in argon matrices has been described in detail previously.[6] In the case of the presently used, poorly volatile compounds, the neutral precursor was placed in a U-tube attached to the inlet

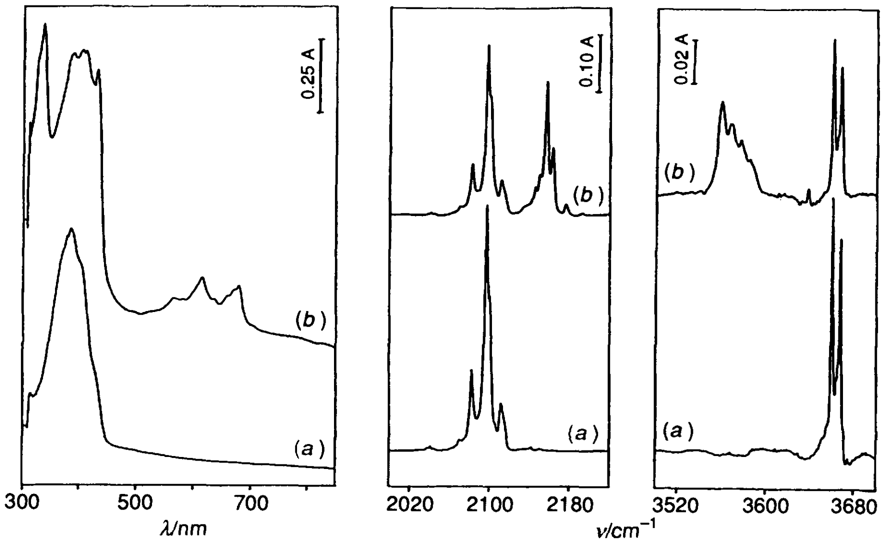


Fig. 1 Changes in the UV–VIS and IR spectra, (*a*) upon photolysis with 313 nm light; (*b*) upon X-ray irradiation of argon matrix-isolated *o*-phthalaldehyde (**1**)

Table 1 Observed vibrational frequencies (cm^{-1}) assigned to the argon matrix-isolated photoenol and its radical cation of *o*-phthalaldehyde

Enol	Radical cation of enol
3667.5m	3584.5m
3660.0m	3574.0m
2112.0m	3568.0m
2100.5s	3559.0m
2097.0s	2177.0w
2082.0m	2163.0s
1628.5w	2157.0s
1539.0w	2150.0m
1217.0m	2146.5m
1150.0vw	1573.0w
1130.0m	1462.0m
753.5m	1373.0w
	1273.0w
	1242.5w
	1234.5m
	1172.0w
	1126.0w
	971.5vw
	738.5w

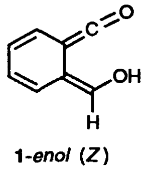
valve where it evaporated slowly into a stream of argon containing 0.1% CH_2Cl_2 (which acts as an electron scavenger). The temperature of the U-tube was adjusted such that the mixture which was deposited over 2 h on a CsI plate held at 20 K contained approximately 0.1% of the neutral precursor. Appropriate temperatures were found to be 0 °C for **1**, +4 °C for **2**, and +55 °C for **3**. After deposition the sample was cooled to the lowest temperature attainable by the close-cycle cryostat (~12 K) whereupon it was exposed to X-rays (40 kV, 40 mA, Tungsten anode) over a period of 2 h.

Photolyses were effected with a 1 kW argon plasma lamp or a 100 W medium pressure Hg lamp using interference filters (313/365 nm) for wavelength selection. UV–VIS spectra were obtained on a Perkin-Elmer Lambda 9 instrument and IR spectra were measured with a Bomem DA3 FT-IR interferometer.

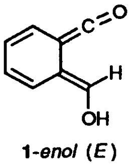
Results and Discussion

o-*Phthalaldehyde*.—Fig. 1(*a*) shows the changes observed in the UV–VIS and IR spectra (ketene and O–H stretching regions) upon irradiation of **1** with 313 nm light. The changes detected in the same spectral regions after X-irradiation of **1** are displayed in the upper traces [Fig. 1(*b*)]. The spectral features in Fig. 1(*a*) are characteristic of the (neutral) photoenol of *o*-phthalaldehyde (**1-*enol***).[3f] Based on the well-documented kinetic behaviour[1,9] and spectroscopic characterization[2c,3f] of the *Z*- and *E*-enols obtained from different *o*-alkyl phenyl ketones and aldehydes, the observed photoenol of **1** can be assigned to the *E*-isomer. Due to the occurrence of two different O–H rotamers and/or matrix site effects, the C=C=O and O–H stretching bands in the IR spectrum are split into several components. All observed vibrational frequencies of **1-*enol*** are listed in Table 1.

The spectra in Fig. 1(*b*) show that **1-*enol*** is also formed in substantial amounts upon X-irradiation but in addition to this we find new bands at 680, 615, 413, 400 and 385 nm in the UV–VIS as well as around 2160 and 3570 nm in the IR spectrum. The former bands are typical for *o*-quinoid radical cations[10] and similar bands were observed earlier after ionization of *o*-methylbenzaldehyde,[2d] 2,4,6-trimethylbenzaldehyde,[2c] *o*-methylacetophenone,[2b] *o*-methylbenzophenone,[2a] as well as 5,8-dimethyltetralone[2b] and were attributed to the corresponding enol radical cations. Concurrently, the new IR bands can be assigned to the ketene and O–H stretching frequencies of **1-*enol***$^{\cdot+}$. As in the case of the *o*-quinoid vinylketene obtained by ring-opening of benzocyclobutenone[10] the ketene vibration is shifted to slightly higher energies upon ionization which is due to the fact that the HOMO of such compounds is C=O antibonding and hence the strength of this bond increases upon removal of an electron. Conversely, the O–H stretching vibrations shifts to lower energies which we explain by a small migration of charge from the O–H bond into the electron deficient π-system of the radical cation. All observed IR bands which we can attribute to **1-*enol***$^{\cdot+}$ are listed in Table 1.



1-*enol* (*Z*)



1-*enol* (*E*)

As in the neutral, the IR bands of **1-*enol***$^{\cdot+}$ are split into several components which indicates formation of several rotamers. In contrast to neutral enols, the *Z*-forms are also stable in the corresponding radical cations, as shown by experiments with 5,8-dimethyl-1-tetralone where only this conformation exists.[2b] A detailed study of *o*-methylbenzaldehyde[2d] has shown that the incipient *Z*-isomer of the enol radical cation actually predominates in the mixture observed after ionization. In that case the *E*-isomer could be enriched by selective photolysis, and we were even able to discern and interconvert different C–OH rotamers with slightly shifted vibrational frequencies. All attempts to induce similar reactions in **1-*enol***$^{\cdot+}$ met with no success and therefore it was impossible to assign the multitude of peaks in the IR spectrum of this compound to different isomers and/or C–OH rotamers.

By analogy with previous cases,[2] we postulate that the mechanism of formation of **1-*enol***$^{\cdot+}$ involves ionization of **1** followed by spontaneous tautomerization of $\mathbf{1}^{\cdot+}$ to the more stable enol radical cation. Conversely, neutral **1** presumably arises as a consequence of the fact that, once formed, **1-*enol***$^{\cdot+}$ effectively competes with CH_2Cl_2 for the electrons ejected from the Ar medium by X-irradiation. This re-neutralization which occurs in all such experiments only leads to perceptible consequences in cases of spontaneous rearrangements of the incipient radical cations such as in the present case of **1**. The yield of such neutral 'photo' products can in fact be substantially higher than upon UV-irradiation.[10] This does not apply for **1** which can be attributed to the fact that all *Z*-enol radical cations immediately reketonize upon re-neutralization and thus effectively disappear from the IR difference spectra. The yield of neutral **1-*enol*** thus depends on the ratio of *Z* to *E* isomer in the corresponding radical cation which is probably in favour of the former.

The sample of ionized **1** proved to be photostable above 550 nm. Irradiation through a 340 nm cut-off filter resulted in bleaching of **1-*enol***$^{\cdot+}$ (an effect which aided in finding the IR bands attributable to this species) as well as the neutral enol and concomitant formation of the neutral secondary photoproducts (phthalide and benzaldehyde) observed previously in N_2 matrices.[3f] Note that these latter products were not detected after X-irradiation which shows that electronic excitation of **1** cannot be responsible for the formation of **1-*enol*** under these conditions.

o-*Nitrobenzaldehyde*.—In Fig. 2(*a*) and 2(*b*) we collected the results of experiments analogous to those described above, this time starting with *o*-nitrobenzaldehyde (**2**). Here, the UV–VIS spectra are less telling and we therefore have to rely entirely on

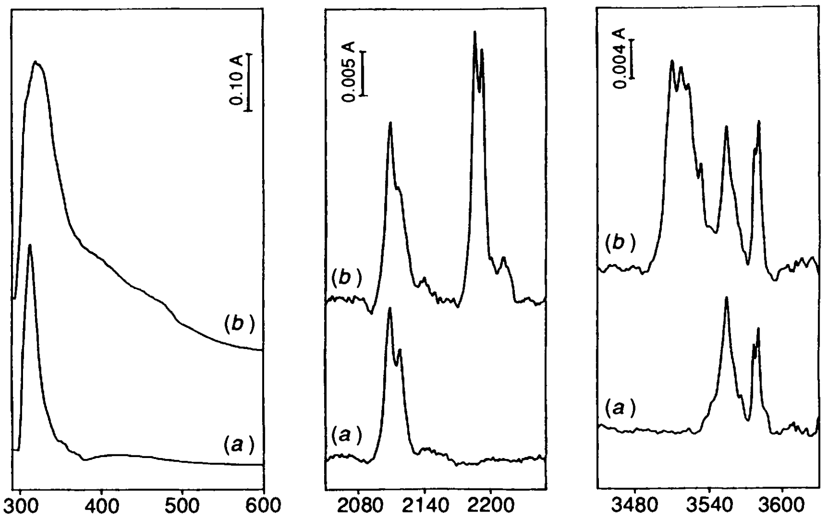
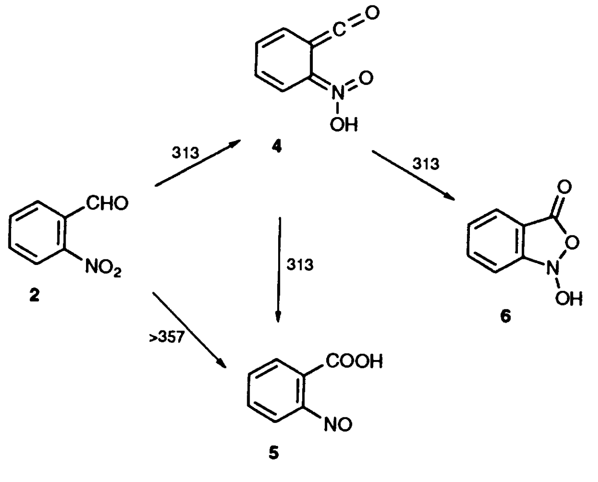


Fig. 2 Changes in the UV–VIS and IR spectra, (*a*) upon photolysis with 313 nm light; (*b*) upon X-ray irradiation of argon matrix-isolated *o*-nitrobenzaldehyde (**2**)

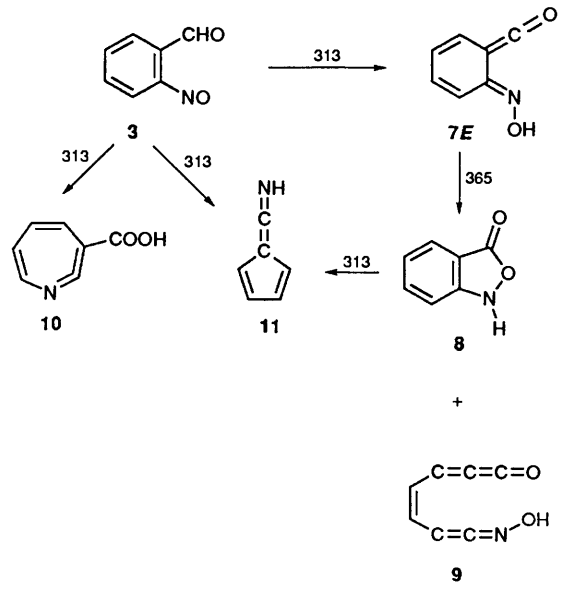
the IR spectra for product identification. The results of short UV-irradiation of **2** (313 nm) are by and large identical to those reported earlier:[4e] we find the C=C=O stretching band of the aci-nitroketene **4** at 2108 and 2115 next to the C=O and OH stretching vibrations of *o*-nitrosobenzoic acid **5** at 1761/1769 and 3553 cm^{-1}, respectively, as well as the pair of sharp OH peaks at 3577/3580 and the C=O band at 1799 cm^{-1} which had been tentatively attributed to *N*-hydroxybenzisoxazolone **6**. By comparison with the closely related aci-nitro isomer obtained from *o*-nitrotoluene, where a pair of peaks at 3525/3527 cm^{-1} was assigned to the N–OH stretching vibration,[11] we surmise that the same vibration is hidden within the broad band between 3530–3570 cm^{-1} in the present case. However, comparison of the intensities of the carbonyl and ketene IR bands shows that only minor amounts of **4** persisted after 313 nm photolysis.



After X-irradiation of **2** we again found the neutral products **5** and **6** in similar concentration as after UV-irradiation. In addition, strong new IR bands at 1738 and 1778 cm^{-1} as well as the multitude of new peaks between 3500 and 3540 cm^{-1} point towards the formation of the corresponding radical cations, **5**$^{\bullet+}$ and **6**$^{\bullet+}$, respectively, which could unfortunately not be positively identified in the present experiments. Next to those we find a pair of peaks at 2186/2192 cm^{-1} which are shifted by 80 cm^{-1} compared to that of the neutral aci-nitroketene and can hence be assigned to the radical cation **4**$^{\bullet+}$. However, the small intensity of this band compared to those arising simultaneously in the carbonyl stretching region (see above) shows that **4**$^{\bullet+}$ is only a minor product of X-irradiation which explains why the distinctive features of the *o*-quinoid π-system could not be clearly detected in the UV–VIS spectra. All bands assigned to radical cations **4**$^{\bullet+}$–**6**$^{\bullet+}$ disappear upon bleaching through a 340 nm cut-off filter.

Thus we conclude that the formyl hydrogen in **2** also undergoes spontaneous migration upon ionization. However, in contrast to the above case of *o*-phthalaldehyde (**1**), other rearrangement products are formed (and subsequently reneutralized) with much greater efficiency which prevents a full characterization of the aci-nitroketene 'enol' cation.

o-Nitrosobenzaldehyde.—Unfortunately, things are even more complicated in the case of *o*-nitrosobenzaldehyde **3** whose photochemistry has recently been explored in some detail,[5] whereby the following processes were postulated to occur:



The UV–VIS and IR spectra of argon matrix isolated **3** after irradiation at 313 nm are shown in Fig. 3(*a*). The IR spectra show the ketene band of oxime **7*E*** at 2093.5/2101.5 cm^{-1} in

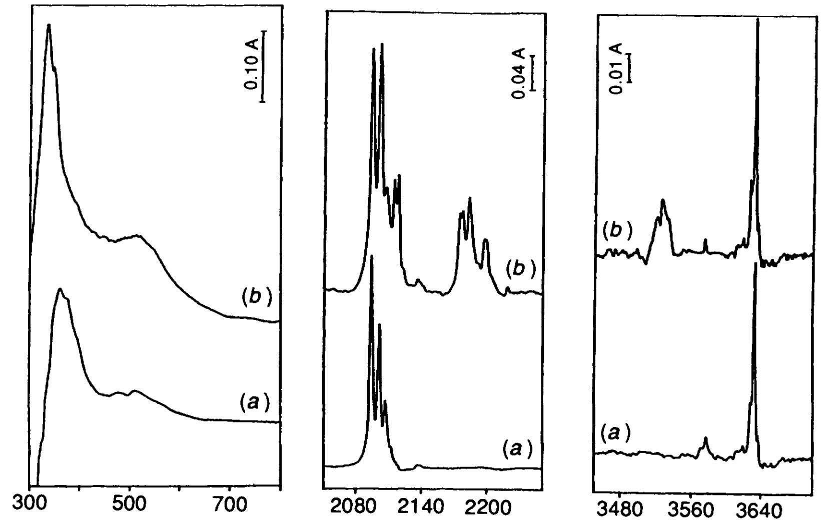


Fig. 3 Changes in the UV–VIS and IR spectra, (*a*) upon photolysis with 313 nm light; (*b*) upon X-ray irradiation of argon matrix-isolated *o*-nitrosobenzaldehyde (**3**)

addition to weaker absorptions of **8** (1799, 1805 and 3305 cm^{-1}), **9** (2029 and 2118 cm^{-1}), **10** (1748, 1889 and 3577 cm^{-1}) and **11** (2043 and 3318 cm^{-1}). Furthermore one can clearly see the sharp OH band of **7*E*** at 3631 cm^{-1}. As in previous cases, we assume that only the *E*-isomer of oxime ketene **7** persists even at 12 K.

In the X-ray experiment [Fig. 3(*b*)] we observe again similar amounts of neutral **7** but more **9** than after UV-irradiation. At high expansions, some bands which were attributed to **10** and **11** can also be discerned. Apart from these, we find a complex new band around 2180 cm^{-1} in addition to new signals at 3515 and 3521 cm^{-1}. This pattern is indicative of ionized **7**, but the multitude of peaks arising within the 2180 cm^{-1} band suggests that perhaps some $\mathbf{9}^{\cdot +}$ contributes also to this signal. However, previous experience implies that both $\mathbf{7}E^{\cdot +}$ and $\mathbf{7}Z^{\cdot +}$ are stable and since both isomers can exist in the form of two stable N–OH rotamers, the complexity of the new IR bands could also be attributed to this.

In contrast to the nitro derivative **2** described in the previous section, the formation of neutral 'enol' **7** is much more efficient in the present case. Unfortunately the yield of ionized ketene oxime $\mathbf{7}^{\cdot +}$ precludes again an analysis of the UV–VIS spectrum in terms of the *o*-quinoid π chromophore also present in this system.

Conclusions

We have shown by UV–VIS and (mainly) IR spectroscopy that spontaneous hydrogen transfer upon ionization is not limited to aromatic carbonyl compounds carrying *o*-alkyl substituents. As in the neutral phototautomerizations, the migrating hydrogen can also originate from a formyl group and the accepting functionality can also be a nitro or nitroso group, but in contrast to the parent neutrals the products of tautomerization (the enol radical cations) are stable with regard to hydrogen back transfer. In the case of nitro- and nitroso-benzaldehyde, formation of side products upon radiolysis (or photolysis) complicates the spectra and precludes the identification of the UV–VIS spectra of the tautomerized radical cations which nevertheless manifest themselves unmistakeably in the IR-spectra.

In all cases of spontaneous hydrogen transfer upon ionization, substantial amounts of the neutral tautomers are formed upon X-irradiation. Those arise presumably by way of re-neutralization of the tautomeric radical ions. In the case of *o*-nitro and nitrosobenzaldehyde, the occurrence of radical ions of various side products could also be inferred from the IR spectra although no attempt was made to identify them.

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