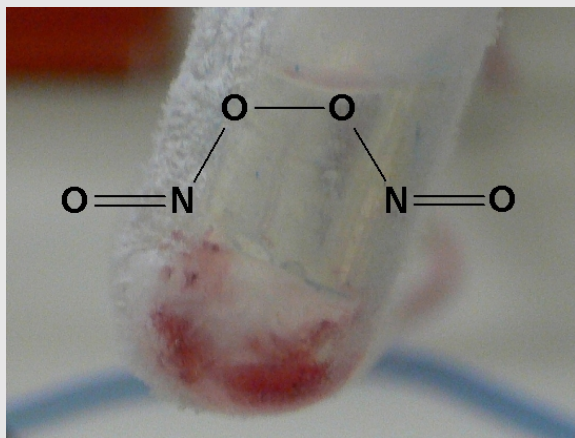


REACTION INTERMEDIATES AT LOW TEMPERATURES: REACTION OF NO• WITH O₂ IN COLD GLASSY HYDROCARBONS

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Cambridge, Massachusetts, USA



ETH

Eidgenössische Technische Hochschule Zürich
Swiss Federal Institute of Technology Zurich

ZEITSCHRIFT FÜR ELEKTROCHEMIE UND ANGEWANDTE PHYSIKALISCHE CHEMIE.

Z. f. Elektroch. Bd. **24.**

1. Juli 1918.

Nr. 13/14 (S. 183—220).

XXIV. Hauptversammlung der Deutschen Bunsen-Gesellschaft für angewandte physikalische Chemie, e. V.

am 8. bis 10. April 1918 in Berlin.

(Fortsetzung von S. 173.)

Herr Prof. Dr. M. Bodenstein-Hannover:

DIE GESCHWINDIGKEIT DER REAKTION ZWISCHEN STICKOXYD UND SAUERSTOFF.

Vor einer ganzen Reihe von Jahren fand in der Zeitschrift für angewandte Chemie eine zum Teil äußerst temperamentvoll geführte Auseinandersetzung statt zwischen den Herren Lunge und Raschig über die Theorie des Bleikammerprozesses¹⁾. In den letzten hierzu-gehörigen Veröffentlichungen teilte zunächst

Herr Raschig¹⁾, dann die Herren Lunge und Berl²⁾ Versuche mit, die eine messende Verfolgung der Vereinigung von Stickoxyd mit Sauerstoff zum Gegenstande hatten. Um diese Messungen an der bekanntlich sehr geschwinden Umsetzung ausführen zu können, war von beiden Seiten so verfahren worden, daß ein Strom von Sauerstoff oder Luft mit einem solchen von

1) Zeitschr. f. angew. Chemie 17, 1398 u. 1777 (1904); 18, 67 u. 1281 (1905); 19, 807, 857, 881 (1906); 20, 694 u. 1713 (1907).

1) L. c. 18, 1281.

2) L. c. 19, 861 u. 1717.

Introduction



Max Bodenstein (1871-1942)

Physical chemist

Made contributions to kinetics
(steady-state assumption) and
reaction mechanisms
($\text{H}_2 + \text{Cl}_2 \rightarrow 2 \text{HCl}$)

Successor to Walther Nernst in
1924 in Berlin

Hermann von Helmholtz-Zentrum für
Kulturtechnik der Humboldt Universität
(Berlin)

Why are we interested?

NO• formed *in vivo*

Given *a*: $\mu\text{M O}_2$ and $\text{nM NO}\bullet$,

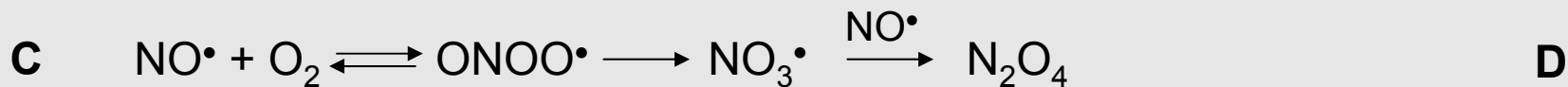
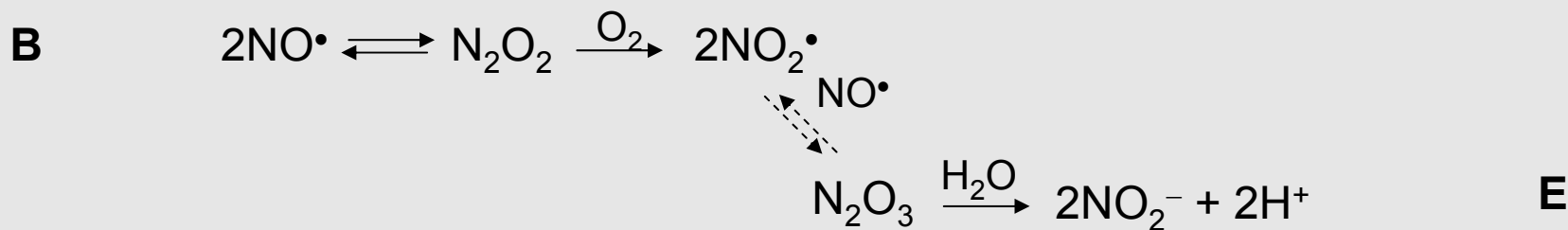
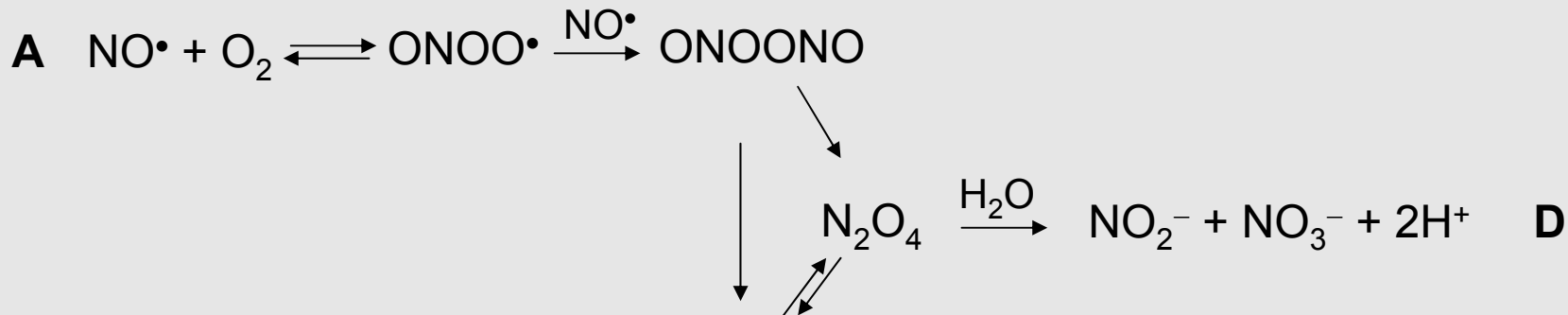
b: ternary reaction,

NO₂• formation takes days!

Yet, nitrosation of thiols is seen

Are there reactive intermediates?

Possible reaction pathways:

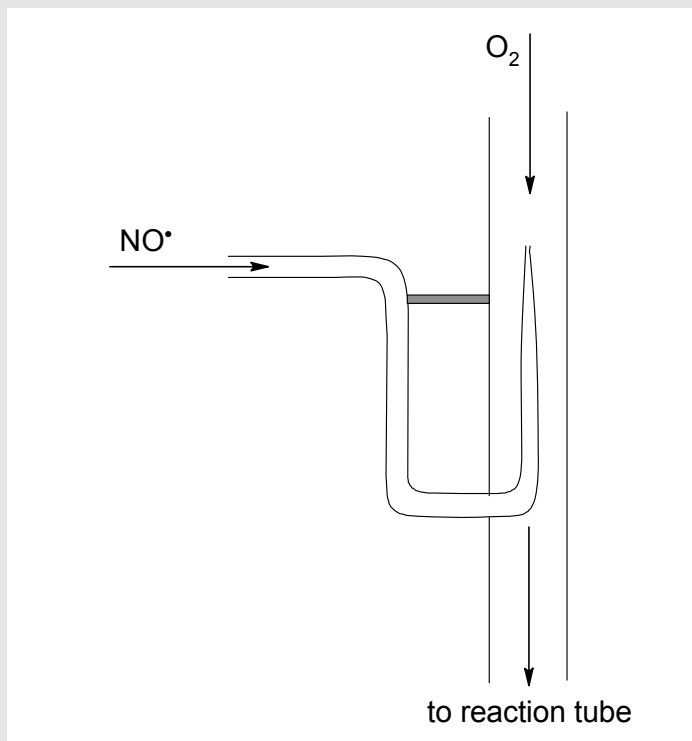


Experimental approach:

1. Determine $\text{NO}_3^- / \text{NO}_2^-$ ratio after hydrolysis
2. Find novel paramagnetic species by gas-phase EPR
3. Observe intermediates during low temperature mixing of O_2 and $\text{NO}\cdot$

1. $\text{NO}_3^- / \text{NO}_2^-$ Ratio after hydrolysis

Gas-flow reactor



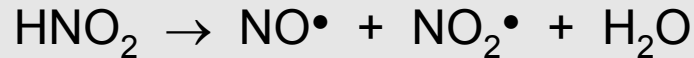
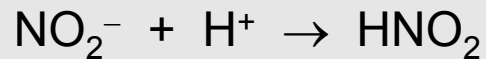
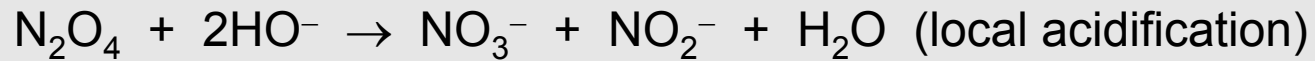
50 – 300 cm, inner \varnothing 6 mm

- O_2 in excess
- Products collected in a cold trap
- Condensates evaporated
- Gas mixture hydrolyzed with NaOH
- NO_3^- and NO_2^- determined by ion chromatography

1. $\text{NO}_3^- / \text{NO}_2^-$ Ratio after hydrolysis

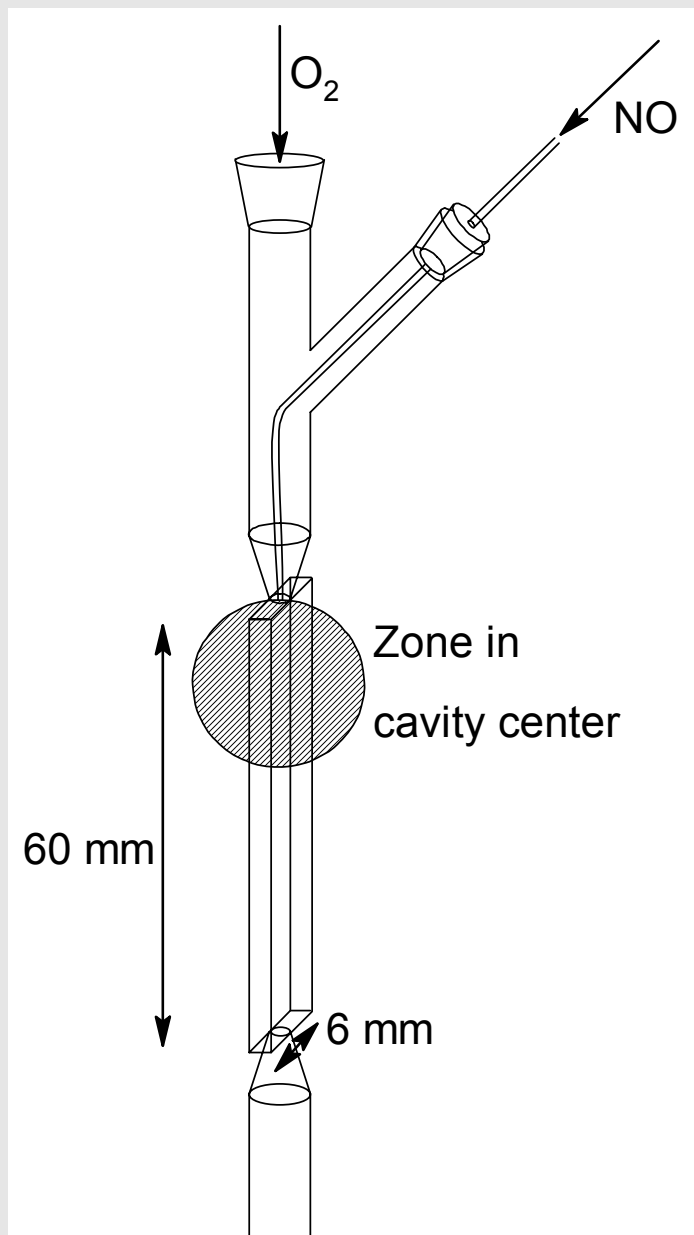
Result: $\text{NO}_3^- / \text{NO}_2^- > 1$

However, apparent excess NO_3^- may actually be attributable to loss of HNO_2 :



$\Rightarrow \text{NO}_3^- / \text{NO}_2^-$ product ratio not a reliable predictor of mechanism

2. Gas-phase EPR of novel paramagnetic species

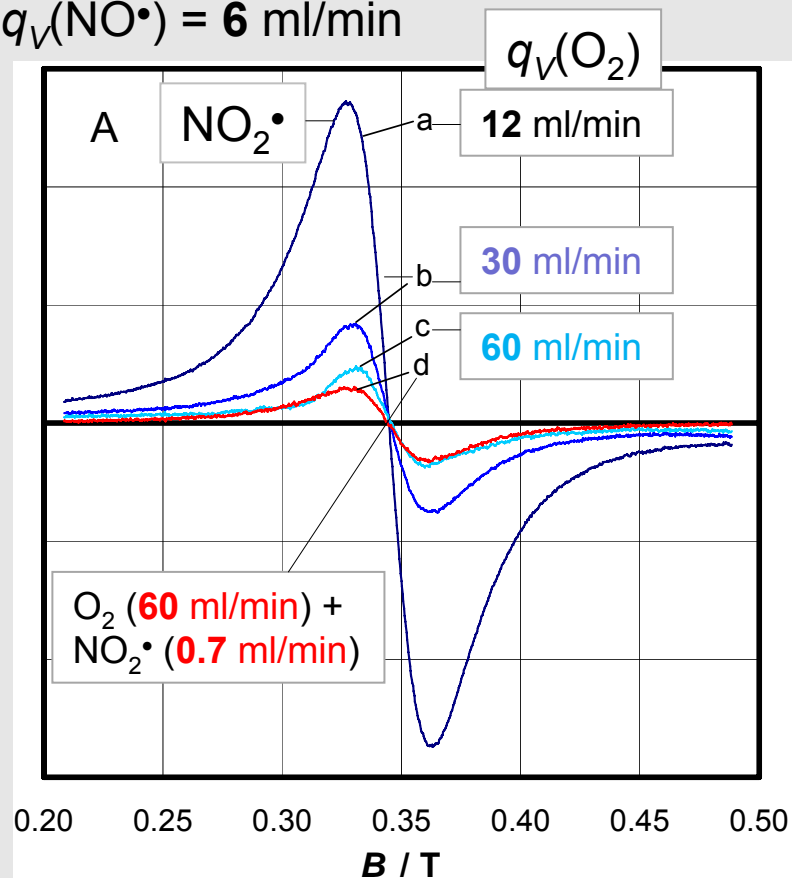


Bruker EMX X-Band EPR spectrometer.

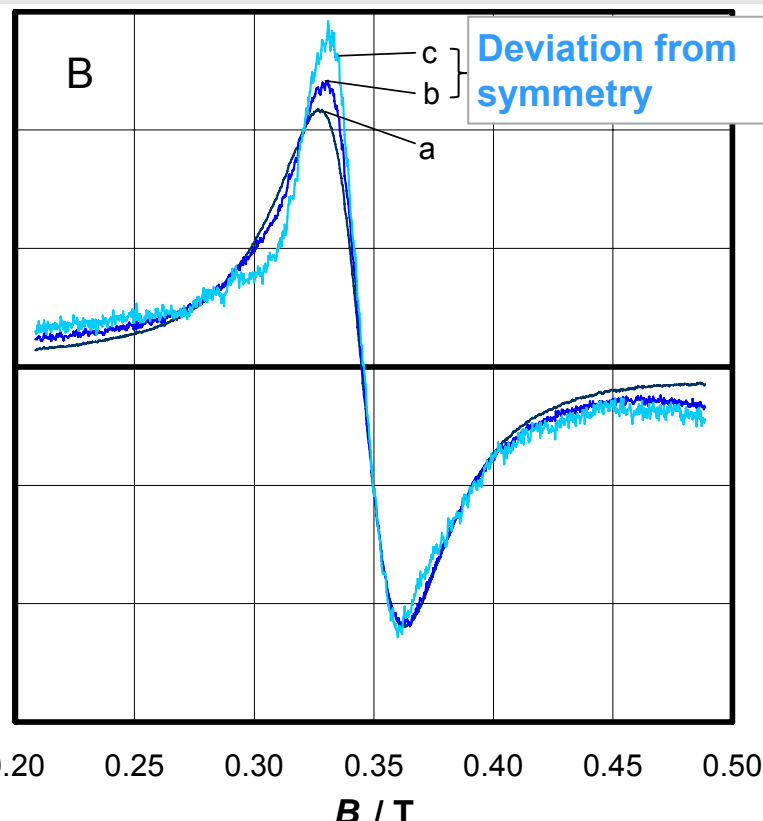
Quartz flat-cell with two inlets

2. Gas-phase EPR of novel paramagnetic species

Gas-flow EPR spectra of $O_2 + NO_2^\bullet$
 $q_V(NO_2^\bullet) = 6$ ml/min



Spectra a–c scaled to equivalent amplitudes (high-field side)



Deviation from symmetry indicates presence of paramagnetic species ($g_{iso} = 2.014$, peroxy radical signature) in addition to NO_2^\bullet ($g_{iso} = 2.000$)

2. Gas-phase EPR of novel paramagnetic species: ONOO•

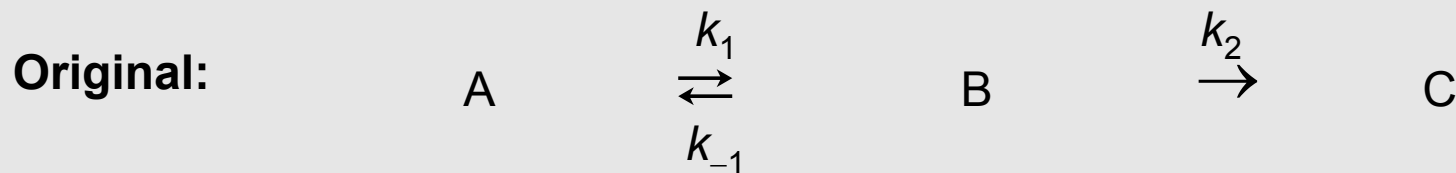
Mole fractions of components in the gas-phase EPR spectra

$q_V(\text{O}_2)$	NO_2^\bullet integral	ONOO^\bullet integral	x_{O_2}	x_{NO}	x_{NO_2}	x_{ONOO}
20	3.41×10^9	4.80×10^6	0.929	0.044	0.0259	3.7×10^{-5}
60	6.87×10^8	1.14×10^7	0.975	0.022	0.0018	3.0×10^{-5}
120	3.71×10^8	2.62×10^7	0.987	0.011	0.0005	3.5×10^{-5}
240	2.20×10^8	3.56×10^7	0.993	0.006	0.0001	2.4×10^{-5}

[a] Spectra collected with the gas-flow reactor cell; flow rate of NO^\bullet fixed at 1.5 mL min^{-1} and flow rate of O_2 variable, given in mL min^{-1} .

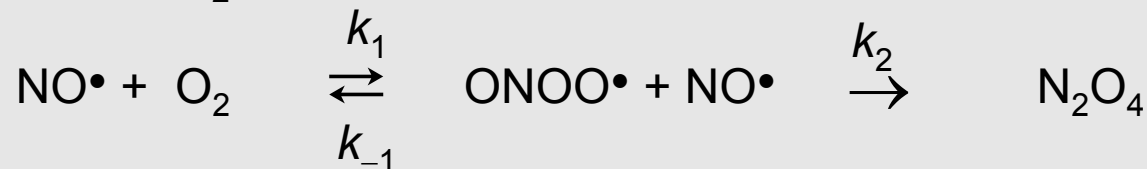
⇒ Proportion of ONOO^\bullet relative to that of NO_2^\bullet increases with flow rate

2. Gas-phase EPR of novel paramagnetic species: ONOO•



Overall kinetics: $\frac{d[C]}{dt} = k_0[A]$ Solution *eigenvalue*: $k_0 = \frac{k_1 k_2}{k_1 + k_{-1} + k_2}$

Modification for NO• + O₂ :



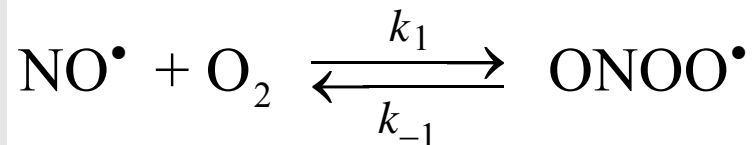
Overall kinetics: $\frac{d[\text{N}_2\text{O}_4]}{dt} = k_{\text{in}}[\text{NO}]^2[\text{O}_2]$

Lindemann, F. A. *Trans. Faraday Soc.* **17**: 598–599; 1922

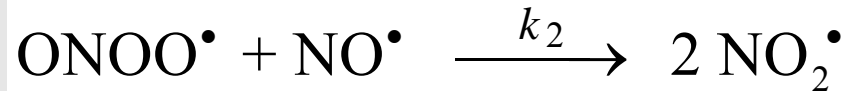
Jachimowski, C. J.; Russell, M. E. *Z. Physik. Chemie Neue Folge* **48**: 102–108; 1966

2. Gas-phase EPR of novel paramagnetic species: ONOO•

Kinetics model



$$k_1 = (80 \pm 50) \text{ s}^{-1}$$
$$k_{-1} = (6.5 \pm 5.5) \cdot 10^3 \text{ s}^{-1}$$

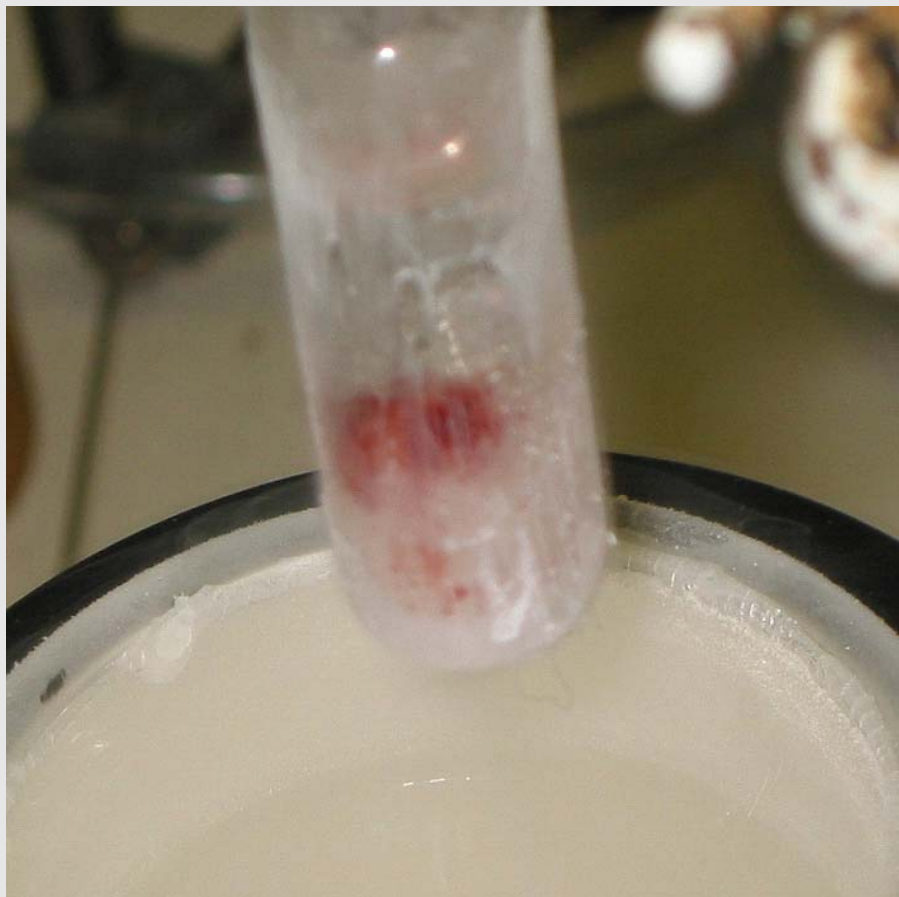


$$k_2 = (1.9 \pm 1.0) \cdot 10^6 \text{ s}^{-1}$$

$$-\frac{dx_{\text{O}_2}}{dt} = k_{\text{tri}} x_{\text{O}_2} x_{\text{NO}\cdot}^2$$

$$k_{\text{tri}} = \frac{k_1 k_2}{k_1 x_{\text{O}_2} + k_{-1} + k_2 x_{\text{NO}\cdot}}$$

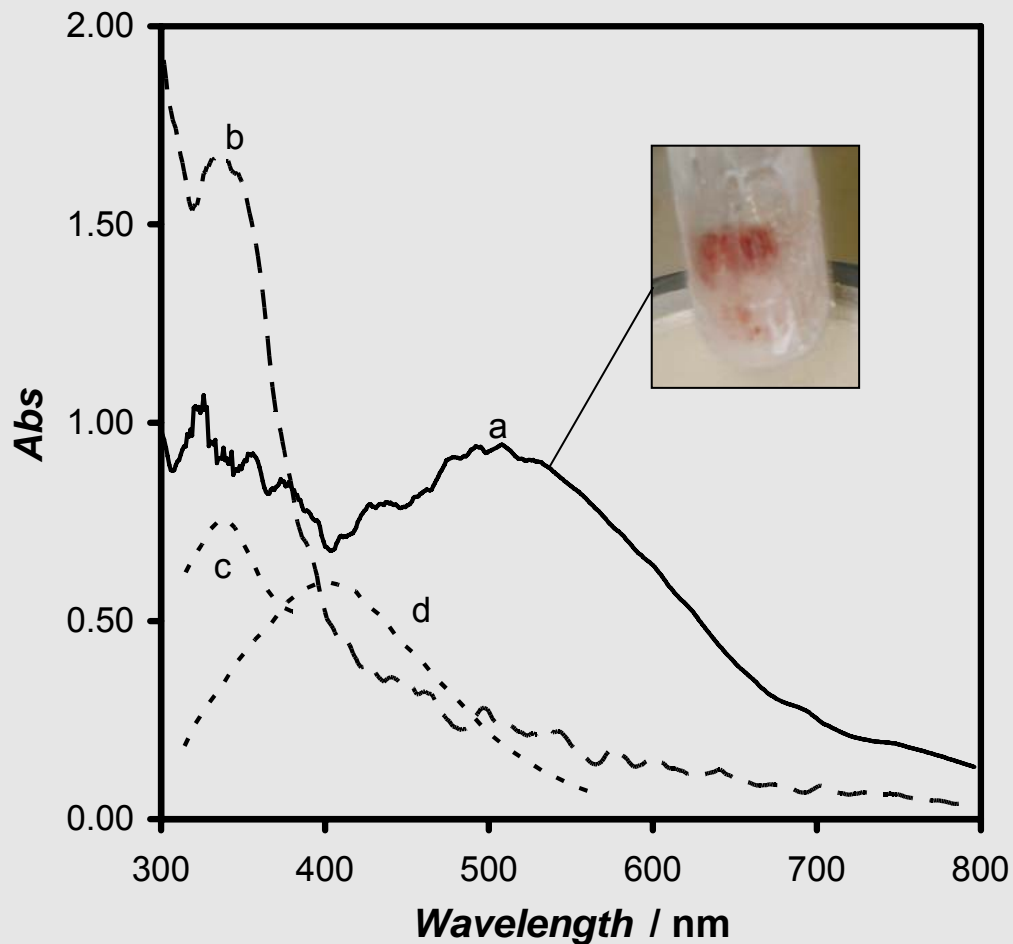
3. Low temperature mixing of O_2 and $NO\cdot$



Upon injection of $NO\cdot$ into O_2 -saturated 2-methylbutane at 113 K, a **red compound** is formed

3. Low temperature mixing of O₂ and NO•

Optical spectrum of the **red compound**



Spectra:

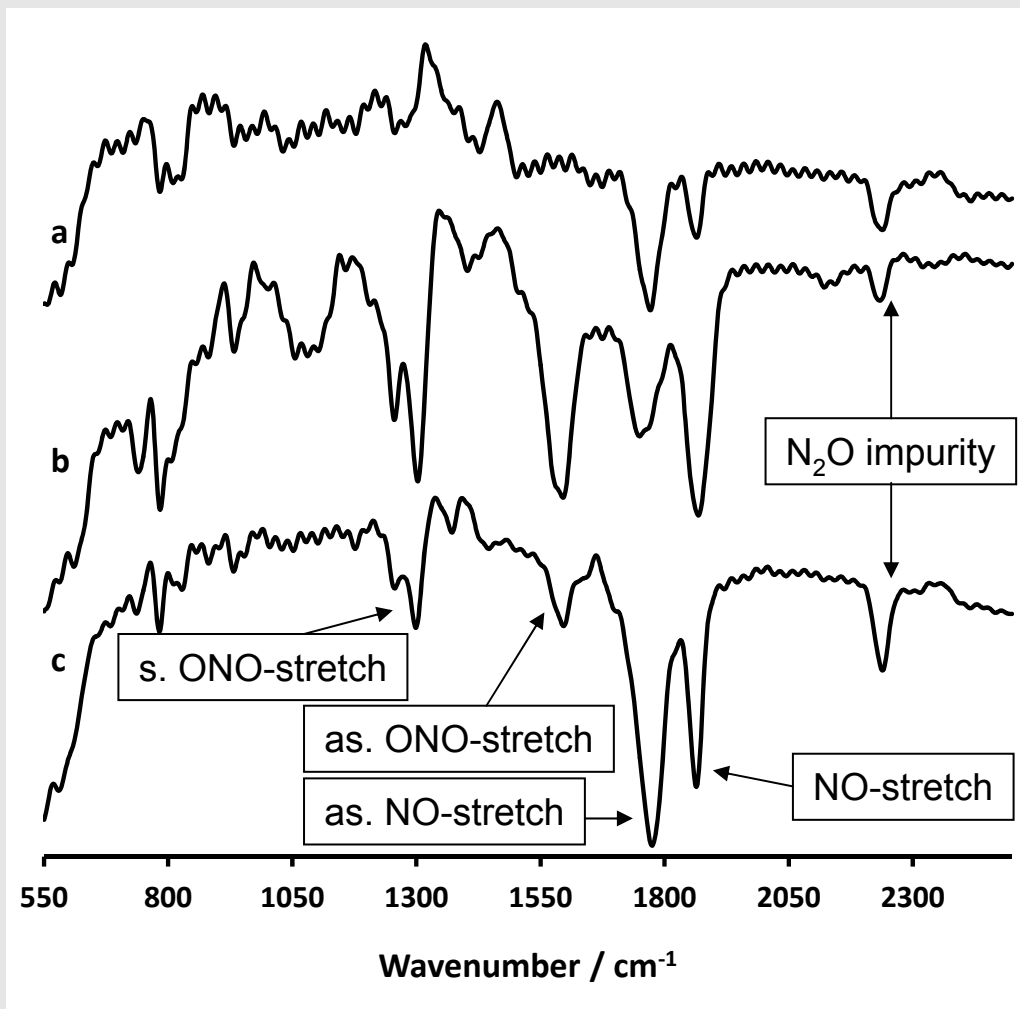
a: at 113 K

b: warmed to 133 K

c: N₂O₄ } literature, reconstructed
d: NO₂• }

3. Low temperature mixing of O₂ and NO•

Infrared spectra in viscous 2-methylbutane at 110 K



Spectra:

a: NO•

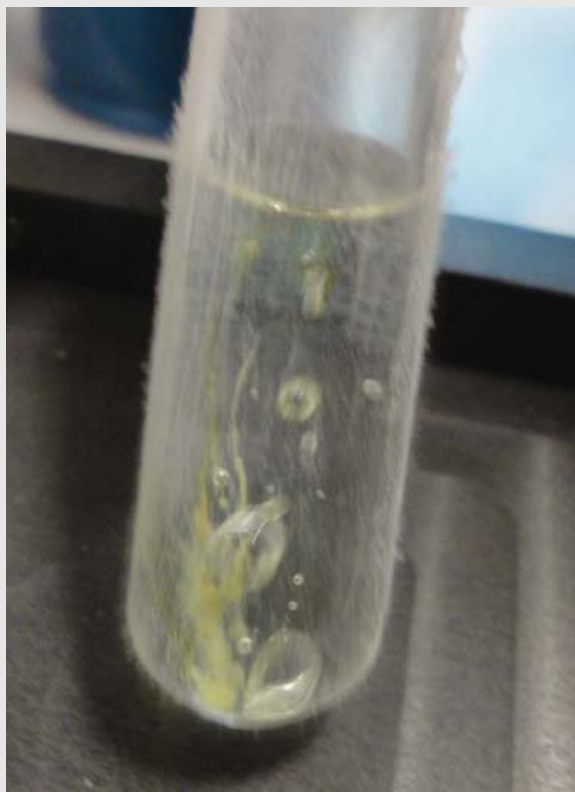
b: NO• + O₂: **red compound**

blue N₂O₃

c: NO• + O₂: **red compound**

⇒ *IR data inconclusive*

3. Even lower temperature mixing of O₂ and NO•



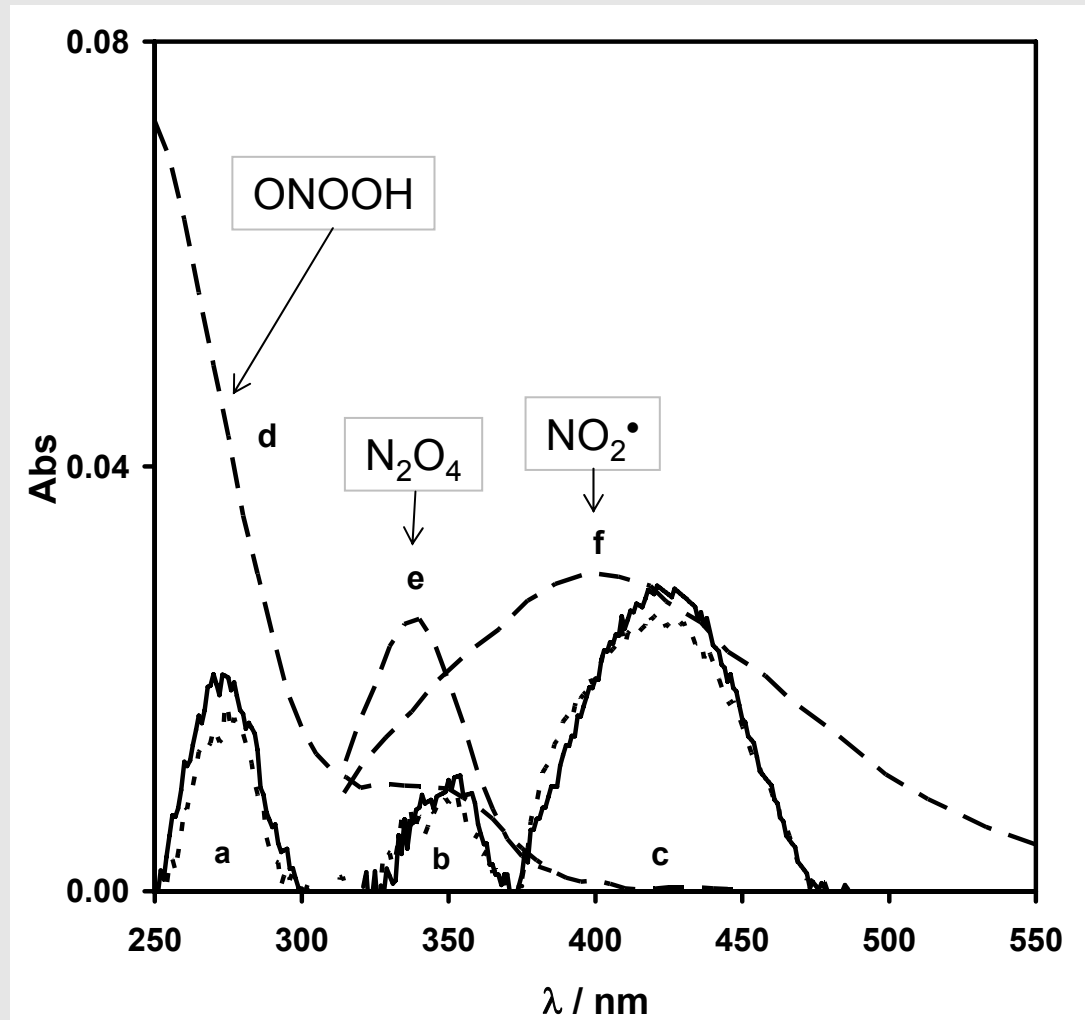
NO• injected into O₂-saturated
“rigisolve” (8:3 2,2-dimethylbutane/*n*-
pentane v/v), 80–90 K → **yellow compound**



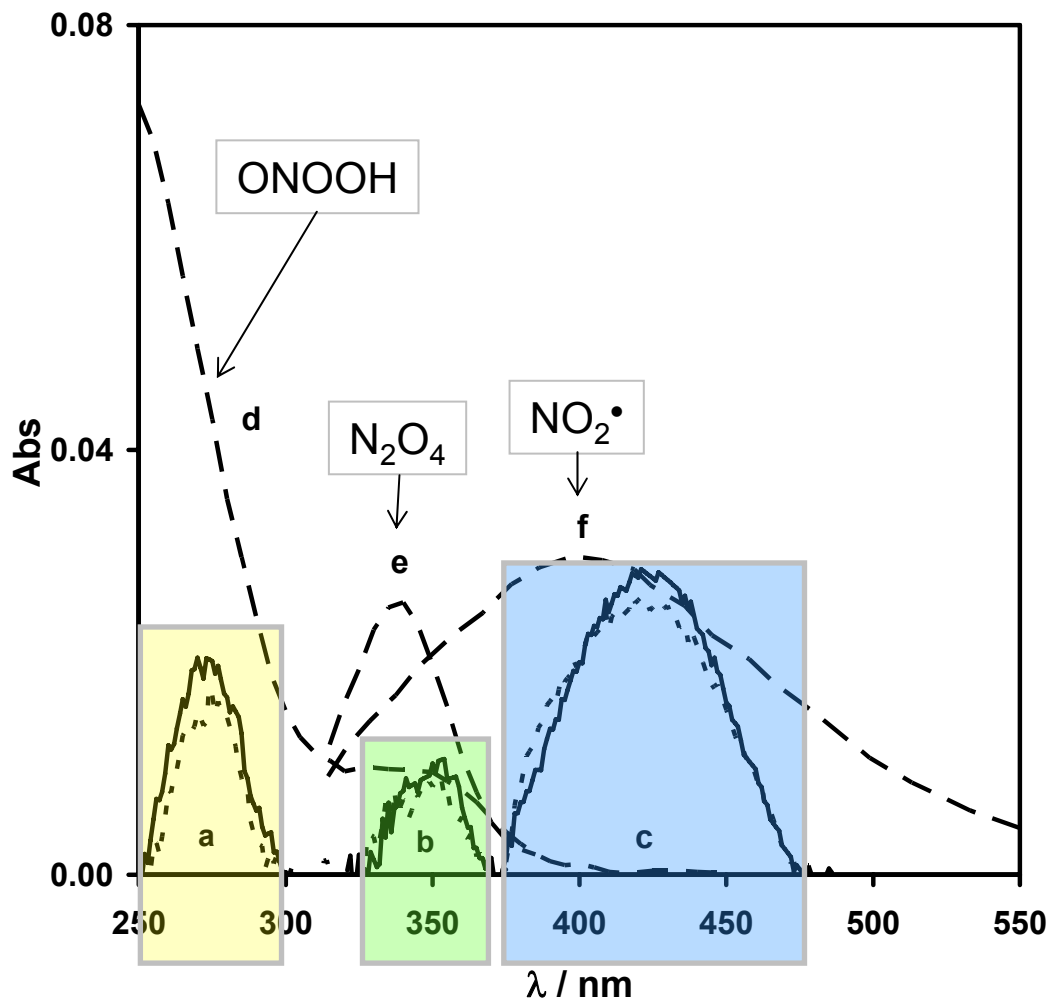
yellow compound

3. Even lower temperature mixing of O₂ and NO•

UV/VIS spectrum of the **yellow compound** (– light scattering background)



3. Low temperature mixing of O₂ and NO•



275 nm:

- Excitation of nonbonding electrons on O next to ONO into the π^* orbital of the ONO group
- Between the strong bands of HOONO (250 nm) and ONOO⁻ (302 nm)
- Consistent with •OONO

425 nm:

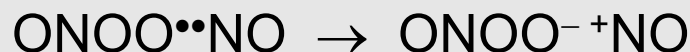
- Charge transfer?

350 nm:

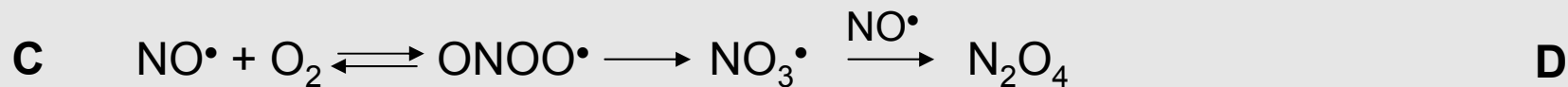
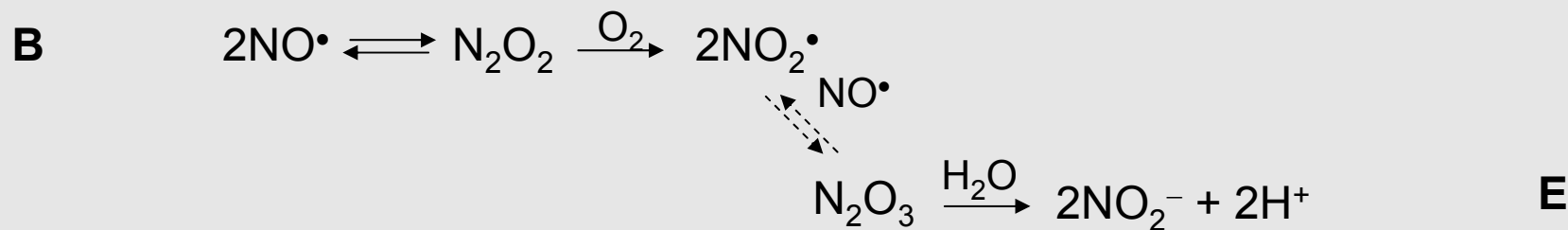
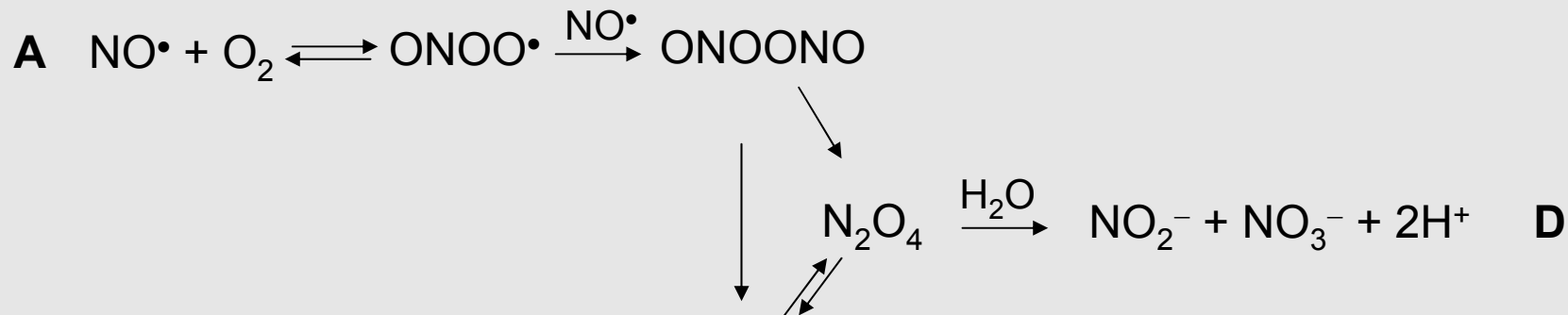
- Consistent with ONO moiety

What is the **yellow compound** ?

- Not paramagnetic
- UV/VIS bands at 275 and 350 nm consistent with $\bullet\text{OONO}$
- Band at 425 nm suggests charge transfer:

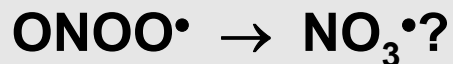


Possible reaction pathways:



A → **D**, so far

Can we exclude **C** → **D**?

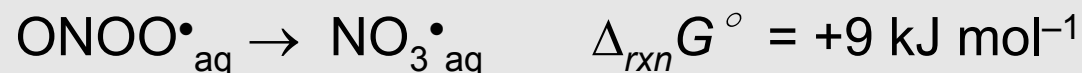


$$\Delta_f G^\circ (\text{ONOO}^-_{\text{aq}}) = 68 \pm 1 \text{ kJ mol}^{-1} \quad (1)$$

$$E^\circ(\text{ONOO}\cdot/\text{ONOO}^-), +0.51 \text{ V} \quad (2) \Rightarrow \Delta_f G^\circ (\text{ONOO}\cdot_{\text{aq}}) = +117 \text{ kJ mol}^{-1}$$

$$\Delta_f G^\circ (\text{NO}_3^-_{\text{aq}}) \text{ of } -111.3 \text{ kJ mol}^{-1} \text{ (NIST)}$$

$$E^\circ(\text{NO}_3\cdot/\text{NO}_3^-) = +2.48 \text{ V} \Rightarrow \Delta_f G^\circ (\text{NO}_3\cdot_{\text{aq}}) = +128 \text{ kJ mol}^{-1}$$



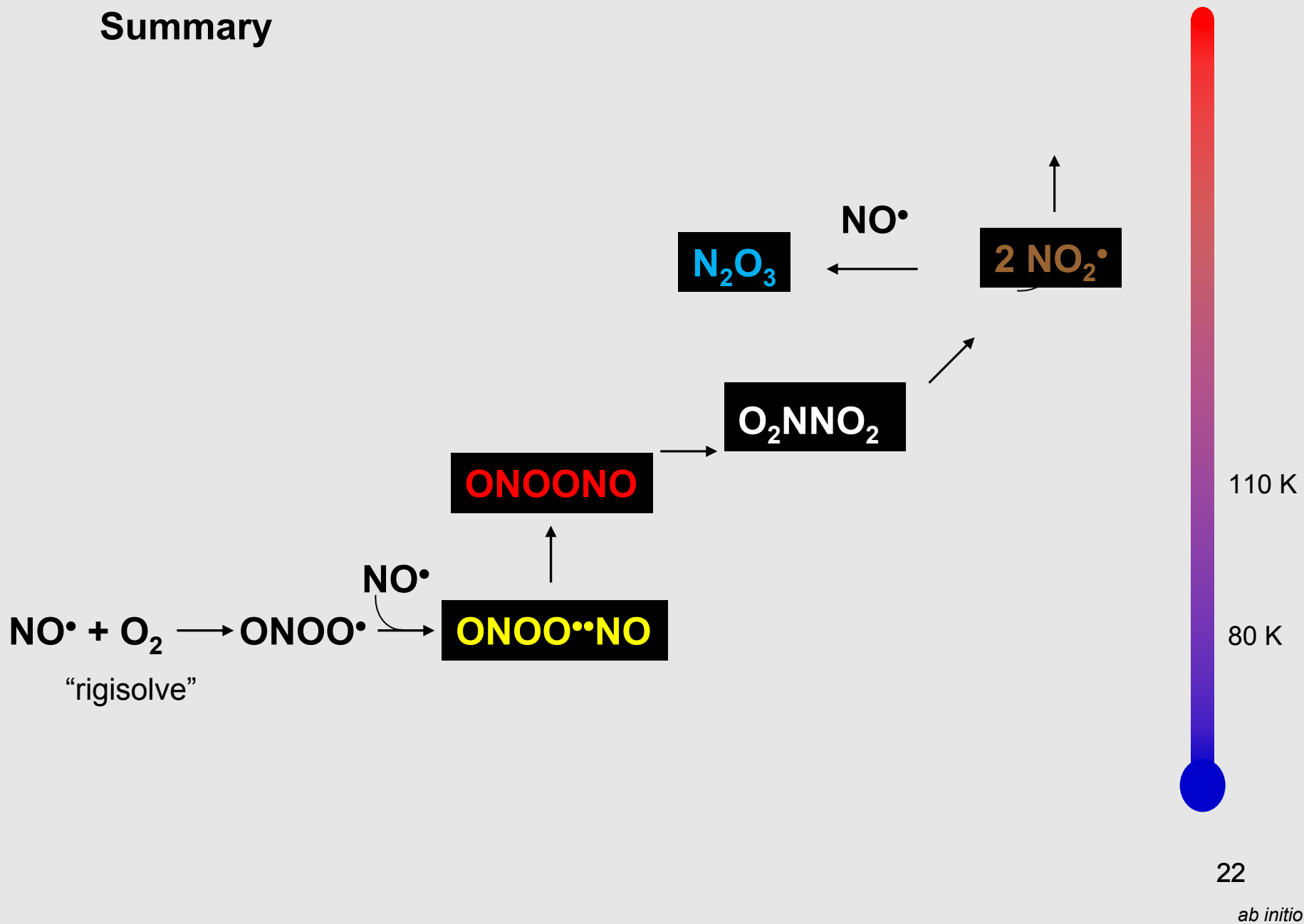
Furthermore, ONOO^- does not isomerize to NO_3^- (very favourable)

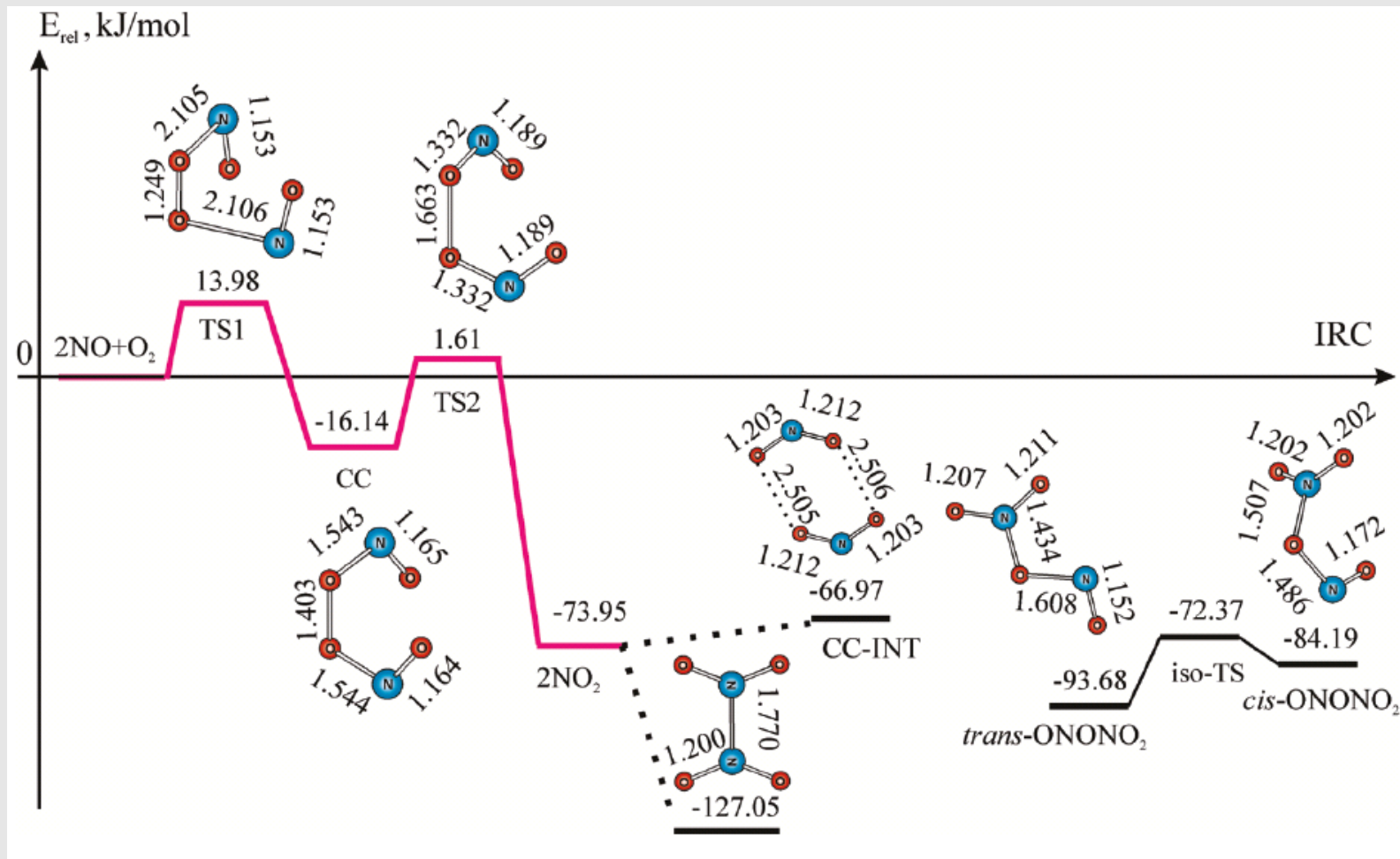
\Rightarrow **$\text{ONOO}\cdot$ is unlikely to isomerize to $\text{NO}_3\cdot$**

(1) Sturzbecher, M.; Kissner, R.; Nauser, T.; Koppenol, W. H., *Inorg. Chem.* **46**: 10655-10658; 2007.

(2) Amatore, C.; Arbault, S.; Bruce, D.; de Oliveira, P.; Erard, M.; Vuillaume, M., *Chem. - Eur. J.* **7**: 4171-4179; 2001.

Summary





Gadzhiev, O. B.; Ignatov, S. K.; Gangopadhyay, S.; Masunov, A. E.; Petrov, A. I., *J. Chem. Theory Comp.* 2011, in press, dx.doi.org./10.1021/ct100754m.



Reinhard Kissner

Leila Mahmoudi

Supported by the ETH and the Swiss Nationalfonds

2. Gas-phase EPR, novel paramagnetic species?

Under the conditions: $[O_2] \gg [NO\bullet]$, $[NO\bullet] \gg [ONOO\bullet]$, $[O_2] \approx \text{constant}$,
and $[NO\bullet] \approx \text{constant}$

substitute: $k_1' = k_1[O_2]$; $k_2' = k_2[NO\bullet]$; $k_{tri}' = k_{tri}[NO\bullet][O_2]$

the pseudo-first-order approach for $NO\bullet$ works only with k_2' !

We define: $\frac{d[N_2O_4]}{dt} = k_{tri}'[NO]$

which can be treated with the original solution formalism to yield

$$k_{tri}' = \frac{k_1' k_2'}{k_1' + k_{-1} + k_2'} = \frac{k_1[O_2]k_2[NO]}{k_1[O_2] + k_{-1} + k_2[NO]} = k_{tri}[O_2][NO]$$

Division by $[O_2][NO\bullet]$ yields the expression $k_{tri} = \frac{k_1 k_2}{k_1[O_2] + k_{-1} + k_2[NO]}$

which is the equation shown on the previous slide.

3. Low temperature mixing of O₂ and NO•

NO• in solid 2-methylbutane	Red product with N ₂ O ₃	Red product	Assignment
2243	2243	2243	N ₂ O impurity
1865	1868	1864	N=O stretch
1771	1750	1775	antisym N=O stretch
	1596, 1581	1601	antisym ONO stretch
	1303	1299	sym ONO stretch
	1256	1256	N ₂ O impurity?