1   **The effect of ozone on nicotine desorption from model surfaces:**

2   **evidence for heterogeneous chemistry**

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7

8   **Abstract**

9   Assessment of secondhand tobacco smoke exposure using nicotine as a tracer

10   or biomarker is affected by sorption of the alkaloid to indoor surfaces and by its long-

11   term re-emission into the gas phase. However, surface chemical interactions of nicotine

12   have not been sufficiently characterized. Here, the reaction of ozone with nicotine

13   sorbed to Teflon and cotton surfaces was investigated in an environmental chamber by

14   monitoring nicotine desorption over a week following equilibration in dry or humid air (65-

15   70 % RH). The Teflon and cotton surfaces had N_2-BET surface areas of 0.19 and 1.17

16   $m^2\,g^{-1}$, and water mass uptakes (at 70 % RH) of 0 and 7.1 % respectively. Compared

17   with dry air baseline levels in the absence of O_3, gas phase nicotine concentrations

18   decrease, by 2 orders of magnitude for Teflon after 50 h at 20–45 ppb O_3, and by a

19   factor of 10 for cotton after 100 h with 13–15 ppb O_3. The ratios of pseudo first-order rate

20   constants for surface reaction (r) to long-term desorption (k) were r/k = 3.5 and 2.0 for

21   Teflon and cotton surfaces, respectively. These results show that surface oxidation was

22   competitive with desorption. Hence, oxidative losses could significantly reduce long-term

23   re-emissions of nicotine from indoor surfaces. Formaldehyde, N-methylformamide,

24   nicotinaldehyde and cotinine were identified as oxidation products, indicating that the

25   pyrrolidinic N was the site of electrophilic attack by O_3. The presence of water vapor had

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1   no effect on the nicotine-O_3 reaction on Teflon surfaces. By contrast, nicotine desorption

2   from cotton in humid air was unaffected by the presence of ozone. These observations

3   are consistent with complete inhibition of ozone-nicotine surface reactions in an aqueous

4   surface film present in cotton but not in Teflon surfaces.

5

6   **Introduction**

7   (*S*)-(-)-Nicotine, the principal alkaloid in tobacco, is emitted in the sidestream and

8   exhaled mainstream smoke of cigarettes (*1*). Owing to its specificity, nicotine is the most

9   commonly used tracer for environmental tobacco smoke (ETS) (*2, 3*), and its metabolite

10   cotinine is the standard biomarker for ETS exposure in epidemiological and intervention

11   studies (*1, 4*). Use of nicotine as a quantitative ETS tracer is supported by the work of

12   Leaderer and Hammond (*5*), in which airborne nicotine correlated (r^2 = 0.64) with fine

13   particle mass when both were measured over weeklong periods in common areas of 47

14   residences with reported smoking. However, it is also known that the dynamic behavior

15   of nicotine differs from that of ETS particles and nonsorbing gases (*6*). Nicotine sorbs

16   rapidly (τ ~ mins) and extensively (>95% sorbed within 2 h) to indoor materials (*7*),

17   greatly reducing concentrations immediately following smoking and creating the potential

18   for exposure after subsequent desorption (*8*). Sorption also limits the spread of nicotine

19   as ETS mixes throughout residences (*9*) and offices (*10*). With repeated smoking,

20   nicotine accumulates on materials and rates of mass desorption increase to yield higher

21   daily "background" concentrations (*11*). Nicotine loading has been measured at tens of

22   μg m^{-2} on hard surfaces (*12*) and estimated at tens of mg m^{-2} for carpet in homes with

23   unrestricted smoking (*13*). Substantial levels of airborne and surface nicotine were

24   measured in the homes of smokers who had previously ceased smoking indoors (*12*).

1   The impact of nicotine sorption on nonsmoker exposures has been studied using

2   indoor air quality models that incorporate this process (*13, 14*). Mathematical models

3   describing nicotine sorption as a fully reversible process have been developed from

4   experimental data collected in room-sized chambers containing one or more common

5   materials (*7, 15, 16*). In these experiments the supply air was directed through activated

6   carbon to remove incoming volatile organic chemicals (VOCs) and produced

7   atmospheres devoid of ozone and other highly reactive compounds. Thus, the potential

8   impact of gaseous or heterogeneous reactions on nicotine sorption was not examined.

9   Nicotine reaction with atmospheric O_2 has been studied under a variety of

10   conditions for the past 90 years, following the seminal 1915 study by G. Ciamician (*17*).

11   Nicotinic acid, myosmine, cotinine, nicotyrine, nicotine-N-oxide, methanone-(1-methyl-3-

12   pyrrolidinyl)-3-pyridinyl and β-nicotyrine have been identified as oxidation products (*18,*

13   *19*). Reaction with O_2 is inhibited in acidified solutions, therefore only the free base is

14   susceptible to oxidation (*20*). Nicotine oxidation by atmospheric ozone (O_3) has not been

15   reported in the literature, but data for structurally related aromatic and aliphatic amines

16   (Table S1, Supporting Information) suggest that nicotine's pyridinic environment is non-

17   reactive and the pyrrolidinic ring may have only moderate reactivity. Using

18   trimethylamine as a surrogate tertiary amine and assuming a typical indoor ozone level

19   of 15 ppb, we estimate a pseudo-first order rate constant of ~10^{-2} h^{-1} for the gas-phase

20   nicotine-ozone reaction. This is roughly 1.5 orders of magnitude lower than typical air

21   exchange rates (*21*), and thus homogeneous oxidation cannot compete with ventilation.

22   The long timescale for nicotine sorption (*7, 11, 12*) suggests the possibility of substantial

23   oxidation by atmospheric ozone through heterogeneous reactions on indoor surfaces.

24   Ozone routinely enters the indoor environment with outdoor air but also may be

25   generated in substantial quantities from devices marketed as "air purifiers" (*22*). It is

26   removed by ventilation and reaction, and indoor levels are typically 20-70% of those

1 outdoors (*23, 24*). Ozone is a major driver of indoor chemistry, and its reaction with

2 common indoor VOCs is a source of irritant chemicals, ultrafine particulate matter and

3 OH radicals (*23, 25*). Ozone reacts with indoor material surfaces (e.g., wallboard and

4 carpet), sometimes yielding secondary pollutants that include volatile aldehydes with low

5 odor or irritation thresholds (*26, 27*).

6   This study examined the hypothesis that atmospheric ozone can react with

7 sorbed nicotine at rates that are significant under typical indoor conditions and that

8 impact nicotine desorption. The potential loss of surface nicotine by heterogeneous

9 reactions has direct and important implications for ETS exposure assessment and

10 modeling. The nicotine-ozone reaction is of interest also because it could yield

11 secondary oxidation products indoors. This concern arises because large quantities of

12 sorbed nicotine are known to be present in homes where habitual smoking has occurred.

13

14 **Methods**

15 ***Chamber design and measurements***

16   We used a bench-scale chamber to directly examine the effect of ozone and

17 relative humidity on nicotine desorption from two well-defined materials: Teflon and

18 cotton. Teflon was studied in the context of characterizing interactions with chamber

19 surfaces and also as a limiting case of a material with low effective surface area and low

20 propensity for uptake of organics and water. Cotton is a ubiquitous indoor material used

21 for clothing, upholstery and draperies. Compared to Teflon, cotton has higher effective

22 surface area and hydrophilicity.

23   Experiments were conducted in a modular chamber constructed with six gypsum

24 wallboard panels (1.2 cm thick) tightly bound by an adjustable metal frame, a design

25 inspired by Wainman et al (*28*). Inner dimensions were 56.3 x 57.0 x 64.0 cm, with a

1   surface area of 2.09 m^2 and a surface to volume ratio of 10.2 m^{-1}. Internal surfaces were

2   covered with FEP-Teflon-lined bench protector. Two inlet ports, located on opposite

3   corners 2-3 cm above the bottom, were used to introduce clean supply air with or without

4   ozone, and nicotine vapor. Air exiting through a single port was directed to a secondary

5   chamber for monitoring temperature and RH. Operationally ideal mixing was verified by

6   offline experiments with SF_6. The chamber was housed in a 70-m^3 lab with mean

7   temperatures of 21.5 - 22.5 ^{o}C and fluctuations of <1.0 ^{o}C during each experiment.

8   A clean air generator fed two supply streams at 5 L min^{-1} (±<1%) each. The

9   primary stream was directed continuously to one of the chamber inlet ports. For

10   experiments requiring humidified air, this stream was bubbled through deionized water.

11   For experiments with ozone, an additional 100 cc min^{-1} fed from a high purity (99.999 %)

12   air cylinder was directed through a UV ozone generator and joined to this primary supply

13   stream. The secondary air stream passed over a diffusion tube containing liquid nicotine

14   (>99%, Aldrich) in a vessel maintained at room temperature in a water bath. The nicotine

15   supply rate, determined gravimetrically, was 0.046 $\pm$ 0.005 mmol h^{-1} throughout all

16   experiments. The nicotine-containing air stream was connected to the second inlet port

17   only during the sorption phase of each experiment; otherwise it was directed to a fume

18   hood. Total airflow to the chamber was 10 L min^{-1} (3 air changes per hour, h^{-1}) during the

19   sorption phase and 5 L min^{-1} (1.5 h^{-1}) during the desorption phase.

20   Ozone was supplied at 0.030-0.033 mmol h^{-1}, corresponding to a steady-state

21   chamber concentration of 56 $\pm$ 3 ppbv in the absence of nicotine and with air exchange

22   at 1.5 h^{-1}. Ozone was measured in the supply air just before and at the conclusion of

23   each experiment using a calibrated UV monitor (API 400). During experiments, ozone

24   was recorded continuously at the chamber outlet every 60 s. Uncertainty in ozone

25   determinations was < 1 ppb.

1   Samples for chemical analysis were collected via a stainless steel 4-port union

2   located just above the outlet port. Nicotine and other organic gases were sampled on

3   Tenax-TA sorbent tubes using peristaltic pumps; sample-specific flow rates were

4   measured to within ±0.5%. Tenax sorbent tubes were analyzed using two thermal

5   desorption-gas chromatography (TD/GC) systems: (1) a Hewlett Packard (HP) 5890

6   equipped with a Perkin-Elmer ATD 400 automatic multi-tube desorber and a nitrogen-

7   phosphorus detector (NPD), or (2) an HP 6890 equipped with a Chrompack TCT 4020

8   desorber with cryogenic trap and a 5973 mass selective detector (MSD) operated in

9   electron impact mode. Operating parameters for the GC-MSD system have been

10   reported (*8*). Nicotine was quantified using multi-point calibrations referenced to internal

11   standards: quinoline for GC-NPD and 1-bromo-4-fluorobenzene for GC-MS. Analytical

12   precision was evaluated with 50 duplicate samples: mean and median standard

13   deviations were 12.9 and 8.6%. Oxidation products were identified using authentic

14   standards (Sigma-Aldrich: N-methyl formamide, 99%; nicotinaldehyde, 98%; cotinine,

15   98%) and spectral libraries.

16   Volatile carbonyls were collected on DNPH-coated silica cartridges preceded by

17   an ozone scrubber. DNPH-coated cartridges were extracted with 2 mL acetonitrile and

18   analyzed by HPLC with diode-array UV-visible detection.

19   The effect on nicotine desorption was examined in a factorial design with three

20   variables (n=8 experiments): surface material (Teflon or cotton), ozone (present or

21   absent) and relative humidity (~0 or 65-70%). Each experiment included conditioning,

22   sorption and desorption phases. The chamber was first conditioned with the primary air

23   stream at the specified RH. The sorption phase began with introduction of the secondary

24   air stream containing nicotine and lasted 12 - 24 h. Nicotine was measured repeatedly to

25   verify that steady-state was achieved at 1.5 - 2.0 ppm (10 - 14 ng mL^{-1}). In some

26   experiments, additional samples were collected to characterize nicotine dynamics during

1   the initial hours of sorption. The desorption phase was initiated by disconnecting the

2   secondary air stream and, in designated experiments, simultaneously connecting the

3   ozone supply. Samples were collected at intervals consistent with the anticipated

4   nicotine concentration change. Samples from selected experiments were analyzed by

5   GC/MS, and chromatograms were screened for the presence of oxidation products.

6   The uncolored, untreated cotton cloth was preconditioned by washing in hot

7   water (no detergent) and machine drying. A rectangular piece (58.2 x 75.5 cm; 85.9 g)

8   was attached to two chamber walls, positioned symmetrically with respect to the outlet

9   and both inlets. For each experiment with ozone, a new section of cloth having the

10   same dimensions (< 0.1 % mass difference) was utilized.

11   ***Surface characterization***

12   The effective areas of exposed Teflon film and cotton cloth were characterized by

13   N_2-BET determination. Small samples of each material (420 and 130 mg, respectively)

14   were conditioned with an N_2 stream in a degasser (FlowPrep 060, Micromeritics) for 24

15   hours. BET-area was measured with a surface gas adsorption analyzer (TriStar 3000,

16   Micromeritics) by sample equilibration over a range of N_2 pressures at 77 K.

17   Water uptake capacity was determined by measuring the mass change of a small

18   sample of each material (roughly 10 cm^2), exposed first to dry air then to air at 70% RH.

19   Material samples were placed in the RH monitoring chamber and equilibrated in 5 L min⁻

20   ¹ dry air for two days, then weighed to quantify dry mass. Samples were replaced in the

21   equilibration chamber and exposed to humidified air for 72 hours; they were removed

22   briefly for weighing at 24, 48 and 72 h. Finally, the samples were exposed to dry air for

23   two days and re-weighed to evaluate hysteresis effects.

1   **Results and Discussion**

2   The primary experimental results are the measured gas phase concentrations

3   during sorption (Fig. 1) and desorption (Fig. 2) phases of experiments with Teflon and

4   cotton. Nicotine concentrations are plotted as circles and squares for dry and humid air,

5   respectively. Solid lines show the patterns for ideal growth and removal by air exchange,

6   i.e. assuming no sorption.

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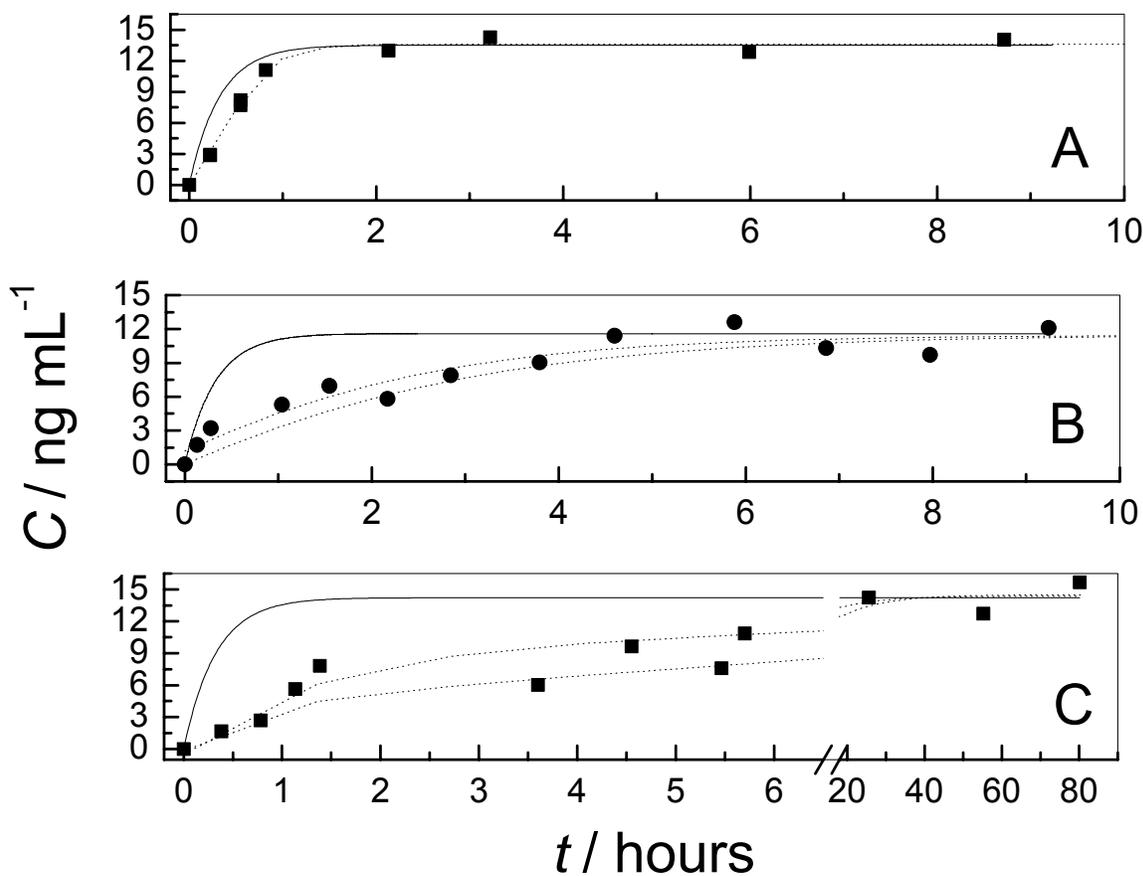
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9   **Figure 1: Nicotine chamber air concentration profiles for (A) Teflon and (B, C) cotton**

10   **surfaces during initial sorption phase under ● dry and ■ humid air. The solid**

11   **curves correspond to the non-sorptive ideal behavior, and the dotted curves to**

12   **fitting of the experimental data showing higher and lower limits.**

1   ***Sorption of nicotine on Teflon and cotton***

2   The extent of sorption is indicated in Figure 1 by the difference between ideal

3   curves and experimental data. The measured nicotine profile differed only slightly from

4   non-sorptive behavior in the Teflon chamber. Substantially more nicotine sorbed when

5   cotton was present (Fig. 1-B and 1-C compared to 1-A). The presence of water vapor did

6   not influence nicotine uptake by Teflon and steady levels were reached within 2 h. With

7   cotton present, steady nicotine concentrations were reached after ~6 h under dry air

8   (Fig. 1-B) and ~15 h under humid air (Fig. 1-C). The mass of nicotine sorbed to surfaces

9   under each condition, M_{sorb} (mg), was estimated using equation 1,

10
$$M_{sorb} = \int_0^{t_{sorb}} f(C_{id} - C)dt \qquad (1)$$

11   where f (m^3 min^{-1}) is airflow through the chamber, $C(t)$ (mg m^{-3}) is the nicotine gas phase

12   concentration, $C_{id}(t)$ (mg m^{-3}) represents ideal, non-sorbing behavior and t_{sorb} (min) is the

13   duration of the sorption phase. Areas under the experimental and ideal non-sorptive

14   curves were calculated numerically and used in equation 1 to obtain M_{sorb} = 0.3 – 0.9 mg

15   for Teflon in humid air, 12-18 mg for cotton in dry air and 33 – 57 mg for cotton in humid

16   air. The midpoints of these ranges suggest that nicotine sorption to cotton was a factor

17   of ~25 (dry air) and ~75 (humid air) greater than sorption to Teflon. Large relative

18   uncertainties in the calculated M_{sorb} values stem from the small difference between

19   experimental and non-sorptive curves for Teflon, and from substantial variability in the

20   measured values in the cotton experiments. This variability is illustrated in Fig 1-B and 1-

21   C which show upper and lower bound estimates for cotton.

22   The substantially higher mass of nicotine sorbed to cotton cannot be explained

23   purely by surface area. The N$_2$-BET surface areas of Teflon and cotton were 0.190 ±

24   0.008 m^2 g^{-1} and 1.17 ± 0.02 m^2 g^{-1}. The result for cotton is similar to literature values for

25   carpet (1.3 m^2 g^{-1}) and a sofa (0.75 m^2 g^{-1}) (*29*), as well as for cellulose powders of

1   varied crystallinity (0.48 – 1.18 m^2 g^{-1}) (*19*). Accounting for the different amount of each

2   material in the chamber, the effective area of cotton was only 3.6 times greater than

3   Teflon.

4   An estimate of maximum surface nicotine coverage can be obtained from the

5   ratio between M_{sorb} and the corresponding effective surface areas. Nicotine surface

6   density for Teflon was 0.02 molecules nm^{-2}, and for cotton (in dry air) was 0.6 molecules

7   nm^{-2}, about 30 times higher. The larger amount of nicotine sorbed to cotton under humid

8   air cannot be directly compared to anhydrous conditions, but it indicates considerable

9   enhancement of sorption due to co-sorbed water. Strong hydrogen-bond interactions are

10   expected when amino groups on nicotine interact with OH groups on the cellulose

11   backbone of cotton. In humid air, greater uptake of nicotine can result from dissolution of

12   the nicotine into aqueous microenvironments present on the surface.

13   ***Desorption of nicotine in the absence of ozone***

14   The filled symbols in Figure 2 show that gas-phase nicotine decreased at

15   approximately the ventilation removal rate (straight line) during the first few hours.

16   Subsequent deviation from the ideal decay curve shows the increasing importance of

17   desorption relative to ventilation removal. With Teflon (Fig 2-A), nicotine gas-phase

18   concentration decreased by 99% before the impact of desorption was apparent. For

19   cotton (Fig 2-B), the measured profile deviated from ideal decay when gas-phase

20   nicotine was >10% of the initial desorption phase concentration. This reflects a

21   substantially higher rate of nicotine desorption (mass transfer to the gas phase) from

22   cotton relative to Teflon. Both materials exhibited ongoing desorption for the entire

23   experimental period. For neither material did desorption appear to be impacted by

24   humidity, even though cotton had absorbed substantial water. By mid-week, nicotine

25   concentrations dropped to about 3 and 2 orders of magnitude below initial levels in

1   Teflon and cotton experiments, respectively. Although both materials were present in the

2   cotton experiments, the effect of cotton dominated and determined the extent of nicotine

3   desorption.
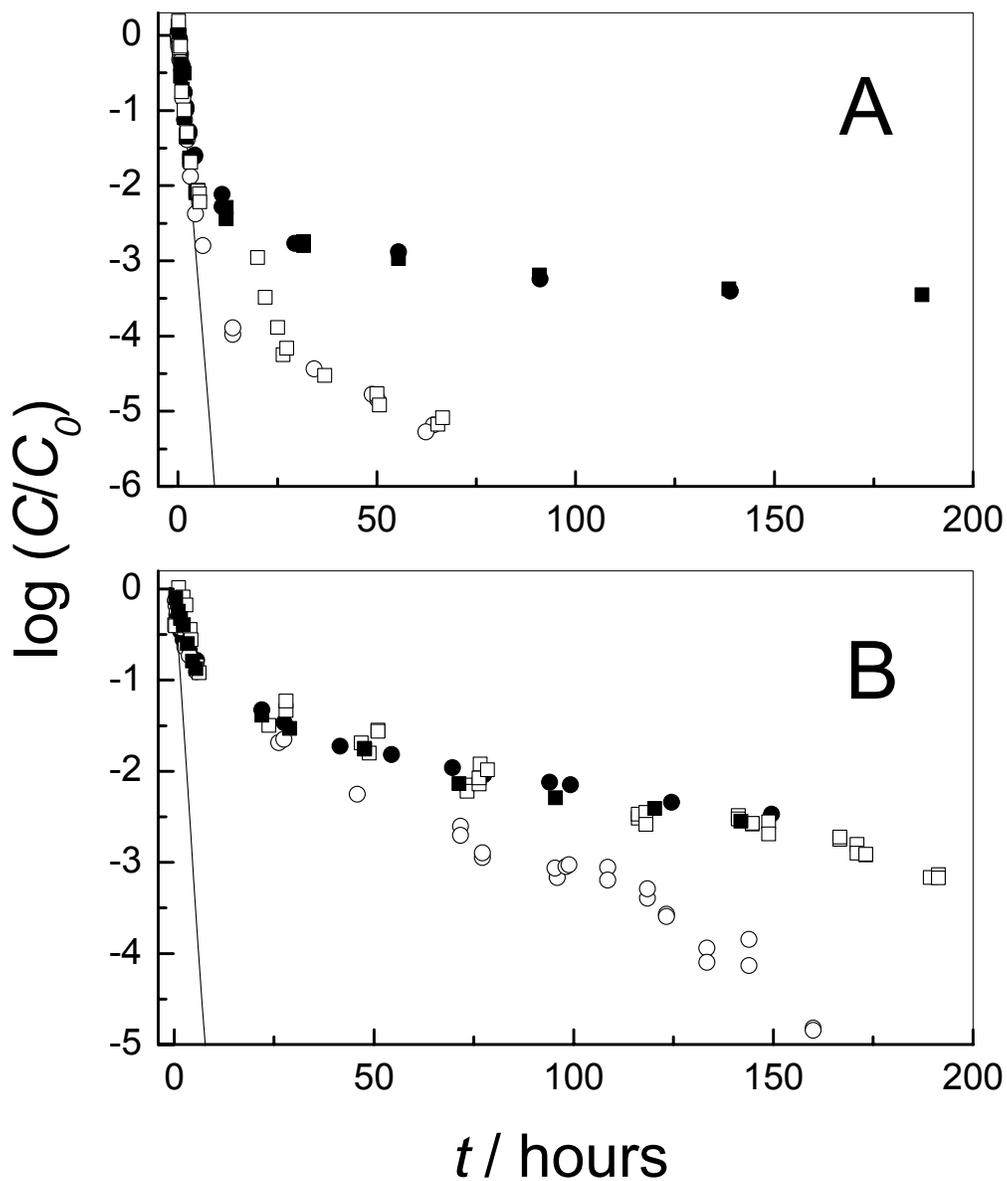
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5   **Figure 2: Nicotine desorption from (A) Teflon and (B) cotton surfaces in ●dry air, no O$_3$;**

6   **■ humid air, no O$_3$; ○ dry air in the presence of O$_3$; □ humid air in the**

7   **presence of O$_3$. The solid curves correspond to the non-sorptive ideal behavior.**

1   Table 1 shows the first order decay coefficients k derived by fitting the natural

2   logarithms of the measured gas-phase concentration profiles in Fig. 2 for $t > 25$ h.

3   Uncertainty was calculated as the standard error of the slope of the fitted line. Gas-

4   phase concentrations during the desorption phase are related to the net mass transfer of

5   nicotine from surfaces; "net" reflects the overall impact of desorption and ongoing re-

6   sorption to materials in the chamber. In four experiments without ozone, decay rate

7   constants were in the range $k = 1.7 – 3.3 \times 10^{-4}$ min^{-1} $(0.25 – 0.5$ day$^{-1})$.

8

9   **Table 1: Initial nicotine gas phase concentration (C_0), desorption rate constant (k),**

10   **pseudo- first order surface reaction rates with ozone (r) and bimolecular**

11   **reaction rates (r^S_{O3}) determined in desorption experiments.**

12

	Teflon		**Cotton**	
	dry air	**humid air**	**dry air**	**humid air**
In the absence of O$_3$				
C_0 (ppm)	1.5 ± 0.1	1.5 ± 0.1	1.6 ± 0.1	1.6 ± 0.1
10^4 k (min^{-1})	2.2 ± 0.6	1.7 ± 0.2	2.7 ± 0.1	3.3 ± 0.3
With O$_3$				
C_0 (ppm)	1.6 ± 0.1	1.7 ± 0.1	1.7 ± 0.1	1.8 ± 0.2
10^4 r (min^{-1})	7.7 ± 0.6	7.3 ± 0.8	5.4 ± 0.4	-
10^5 r^S_{O3} (ppb^{-1} min^{-1})	1.8 ± 0.3	1.7 ± 0.3	3.8 ± 0.5	-

13

14   Relative humidity had minimal influence on the desorption profiles from both

15   materials (Fig 2), despite considerable water uptake by cotton. While Teflon did not

16   show any measurable mass change, the cotton mass increased by 7.1 ± 0.3 % when

1   exposed to ~70 % RH. This uptake is consistent with the mass change reported for a

2   cotton sample exposed to the whole humidity range (*30, 31*).

3   The mass of nicotine desorbed during each experiment was calculated as:

4    $$M_{des} = \int_0^{t_{des}} fCdt - C_0V \qquad\qquad (2)$$

5   where t_{des} (min) is the duration of the desorption phase, and the product C_0V (mg)

6   corresponds to the mass present in the gas phase at $t = 0$. For Teflon surfaces, the

7   calculated M_{des} = 0.4 – 0.6 mg for experiments in dry and 0.5 – 0.7 mg in humid air are

8   within the range estimated for sorbed mass M_{sorb}. For cotton, the calculated masses of

9   desorbed nicotine were 12 - 16 mg in dry air and 11 - 15 mg in humid air, compared to

10   M_{sorb} = 12-18 and 33-57 mg sorbed in dry and humid air respectively. This indicates that

11   in dry air most of the sorbed mass was desorbed within a week, whereas in humid air,

12   less than half was desorbed over the same period. The time required to desorb most of

13   the remaining mass is projected to be on the order of several months.

14   ***Effect of ozone on nicotine desorption***

15   The presence of ozone affected markedly the desorption profiles shown in Figure

16   2 (open symbols). A dramatic change in the nicotine concentration profiles was observed

17   with Teflon surfaces (Fig. 2-A) in both dry and humid air. After one day of desorption,

18   gas-phase nicotine levels in the presence of ozone were more than 10 times lower than

19   those recorded without ozone. Gas-phase nicotine levels were nearly 2 orders of

20   magnitude lower after the second day and below limits of detection after 70 hours.

21   Ozone influenced nicotine desorption from cotton (Fig 2-B) in dry but not humid air

22   conditions. Relative to no-ozone conditions, gas-phase nicotine levels were lower by an

23   order of magnitude after ~100 h in dry air.

24   Ozone curves corresponding to the same experiments are shown in Figure S1.

1   The observed gas-phase nicotine concentration decline in the presence of ozone

2   cannot be explained by gas-phase reaction. The most direct evidence of this is the

3   disparity in results for cotton. If homogeneous reaction accounted for the nicotine

4   reduction in dry air, then it should have caused a significant reduction in humid air as

5   well. The lack of significant homogeneous reaction is consistent with the rate inferred

6   from trimethylamine data (see Introduction), which is 2 orders of magnitude slower than

7   the chamber air exchange rate.

8   We postulate instead that the observed reduction in gas-phase nicotine resulted

9   from heterogeneous reactions which reduced the amount of nicotine re-emitted from the

10   surface. The different results for cotton under dry vs. humid air are attributed to the role

11   of co-sorbed water as an inhibitor of the heterogeneous nicotine-ozone reaction. We

12   expand and explore this hypothesis below.

13   A simple kinetic scheme for gas phase (*C*) and sorbed (*S*) nicotine in the

14   presence of ozone is given by:

15
$$\frac{dC}{dt} = -\lambda.C + \frac{A}{V}kS \qquad (3)$$

16
$$\frac{dS}{dt} = -kS - rS \qquad (4)$$

17   where λ is the air exchange rate, *A* and *V* are the chamber area and volume, *k* (min^{-1}) is

18   the net desorption rate constant, and *r* (min^{-1}) the pseudo first-order rate constants for

19   reaction between surface nicotine and ozone at a steady gas phase concentration. For

20   cotton experiments, equations 3-4 strictly should include terms for both cotton and the

21   Teflon-coated chamber walls. However, since ~96 (dry air) and ~99% (humid air) of the

22   sorbed nicotine was associated with cotton, the impact of Teflon was taken as negligible

23   and a single *S* was used. Equations 3-4 were solved analytically to obtain this

24   expression for gas-phase nicotine C(t) as a function of time:

1 $$C(t) = C_0 \exp(-\lambda t) + \frac{A}{V} \frac{k}{(\lambda - k - r)} S_0 \{\exp[-(k+r)t] - \exp[-\lambda t]\} \qquad (5)$$

2 with C_0 and S_0 the initial nicotine concentration in each phase. For $t > 25$ h, the

3 parameter $(k + r)$ can be calculated directly from the slope of the ln (C/C_0) vs t curves in

4 the same way as k was calculated above in the absence of ozone, provided that $(k + r)$

5 $<< \lambda$. Hence, steeper decays in experiments with ozone, compared to no-ozone

6 experiments, are attributed to reaction.

7   The ratio r/k gives a quantitative measure of the relative rates for the competing

8 processes of desorption and reaction with ozone. Results in Table 1 suggest that

9 heterogeneous reaction with ozone reduced desorption from Teflon surfaces at $r/k = 3.5$

10 (dry air) and 4.2 (humid air) times the rate of removal by ventilation. For cotton surfaces

11 in dry air, heterogeneous ozone reactions reduced gas-phase concentrations during

12 desorption at twice the rate accomplished by ventilation removal alone ($r/k = 2.0$).

13 Uncertainty was calculated from the standard error of the slope of the fitted line.

14   The pseudo-first order reaction rate r can be seen as the product of a bimolecular

15 rate constant r^S_{O3} (ppb^{-1}min^{-1}) for the reaction between ozone and surface-sorbed

16 nicotine, and a stable gas-phase ozone concentration [O$_3$] (ppb):

17 $$r = r^S_{O3}[O_3] \qquad (6)$$

18 Bimolecular rate constants were calculated for ozone reacting with nicotine sorbed to

19 Teflon or cotton using average O$_3$ concentrations of 42 and 14 ppb, respectively. The

20 value of r^S_{O3} for Teflon was only half of that for cotton under dry air (Table 1). Thus,

21 sorption of nicotine to the more strongly interacting substrate (cotton) did not increase

22 protection of the sorbate from oxidation by atmospheric ozone in dry air.

23   Okubayashi et al (*31*) determined that a monolayer of water was established on

24 cotton in equilibrium with 30-40 % RH. At our higher RH conditions, the cotton surface

1   held more than one layer, and water also accumulated in aqueous microenvironments or

2   "pools". The protective role of co-sorbed water at ~70% RH could be due to either or

3   both of these reasons:

4   1) Ozone decomposes in aqueous media, catalyzed by OH^- at pH > 6 (*32*). This

5   reaction is also surface-catalyzed (*33*). In humid air and in the absence of nicotine (blank

6   curve in Fig. 1S-B), cotton consumed ozone at the mass transport limited rate during the

7   initial 5 days. The presence of the alkaloid in the surface aqueous film may further

8   contribute to the OH^- catalyzed O_3 depletion by providing a more basic medium.

9   2) Nicotine can be protected by reversible chemical association with co-sorbed

10 water. Protonation of its amino groups or hydrogen bonding make nicotine less

11 susceptible to electrophilic attack. In dilute aqueous solution, nicotine is preferentially

12 protonated in the methylpyrrolidinic N atom at pH lower than pK_1 = 8.01, and can only

13 exist in the diprotonated form at pH near or below pK_2 = 3.10. Pankow et al. (*34*) showed

14 that the acid-base behavior of nicotine was not significantly altered in systems with lower

15 aqueous activity, such as water glycerin (35/65) mixtures, with respect to pure aqueous

16 solution.

17 ***Nicotine-ozone surface chemistry***

18   We investigated the formation of stable oxidation products during desorption

19 experiments. Figure 3 shows the gas-phase concentrations of N-methyl formamide,

20 nicotinaldehyde (or 3-pyridinecarboxaldehyde) and cotinine for Teflon (A) and cotton (B)

21 surfaces, along with the nicotine levels for the same experiments, performed in the

22 presence of ozone in dry air. These species were not detected in the absence of ozone.

23 On Teflon, the concentrations of oxidation products decreased steadily as surface

24 nicotine was depleted, while the levels of oxidation products generated at cotton

25 surfaces were relatively constant during the desorption period. This is consistent with

1   higher nicotine surface concentration present on cotton surfaces and with the stability of

2   ozone levels during the cotton exposure, suggesting a quasi steady-state for the surface

3   reaction.

4
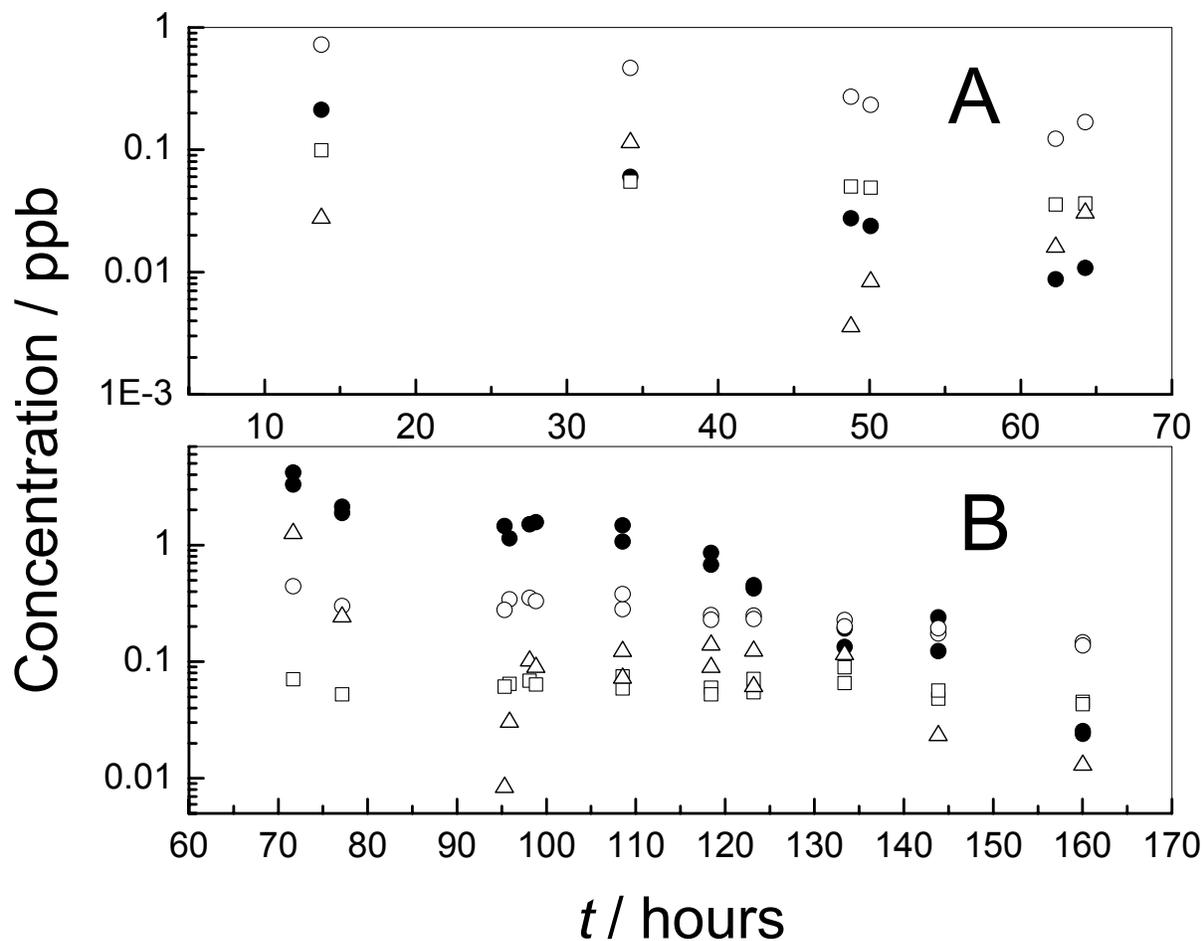
5
6

7   **Figure 3: Gas-phase concentration of nicotine oxidation products in (A) Teflon and (B)**

8   **cotton experiments performed with dry air in the presence of ozone: ○ N-**

9   **methylformamide; □ nicotinaldehyde; Δ cotinine. Nicotine concentrations (●)**

10   **are also indicated.**

1   Formaldehyde formed during ozone interaction with nicotine on both surfaces.

2   Extracts of DNPH-impregnated samplers collected during the Teflon/humid air

3   experiment over the periods 6-20 h and 20-29 h yielded formaldehyde levels of 1.9 and

4   1.8 ppb respectively. Similarly, samples collected during the cotton/dry air study showed

5   higher (4.1 ppb) levels during the first day of desorption (2-5 h), and fell to 1.9 ppb at the

6   end of the period (97-101 h). Formaldehyde concentrations in the blanks were negligible

7   for Teflon, but were in the order of 0.7 and 0.6 ppb for blanks collected in the presence

8   of cotton from 3-5 h and 5-19 h, respectively. This is an indication of reactions of the

9   cotton with ozone, or with ozone-related reactive species such as OH radical.

10   The measured levels of oxidation products were comparable or higher than

11   residual nicotine levels, in particular for VOCs of concern such as formaldehyde or N-

12   methylformamide.

13   The molecular structures of stable products of nicotine ozonation (solid box) and

14   tentatively identified myosmine (dotted box) are shown in Figure 4. While our

15   experimental evidence strongly supports the hypothesis that primary steps of ozonation

16   take place on the surface, some of these products may be formed in subsequent

17   reaction steps in the surface or in the gas phase. Postulated intermediate radical species

18   were adapted from the mechanism described by Tuazon et al (*35*) for ozone-

19   trimethylamine gas-phase reactions. Ozonation mechanisms of tertiary amines in

20   aqueous solution share the same principles (*36*). An initial electrophilic attack of ozone

21   at the amino group yields an excited *N*-oxide that can decompose via CH_3 or OH loss.

22   The first process leads to the formation of stable nitro and nitroso compounds (not

23   investigated) and oxidation products of the CH_3 radicals, including formaldehyde. The

24   second pathway leads to the formation of two organic radicals, indicated as (**I**) and (**II**) in

25   Fig 4. Reaction with O_2 and recombination lead to various possible stable oxidation

26   products. Additional multifunctional reaction products were tentatively identified by

1   matching their mass spectra with library data. Those structures, presented in Figure S2,

2   probably originate in oxidation and fragmentation of the structures shown in Figure 4.

3   The observed reaction products derive from ozone attack on the pyrrolidinic ring

4   of nicotine. This observation lends support to the hypothesis that nicotine interaction with

5   the aqueous environment at the surface interferes or protects against ozone oxidation,

6   because both take place at the pyrrolidinic amino moiety. Acid-base or other molecular

7   interactions that induce a change in the electron density on that group can effectively

8   inhibit oxidation reactions that operate through electrophilic attack on the pyrrolidinic

9   nitrogen atom. Muñoz and von Sonntag (*37*) described a detailed mechanism for the

10   initial steps of the reaction of ozone with tertiary amines in aqueous solution, observing

11   that only the free base reacts with O_3 at rates in the order of 10^6 L mol^{-1} s^{-1}.

12   ***Relevance to real indoor environments***

13   We have shown that surface ozone chemistry can dramatically reduce nicotine

14   desorption rates and account for the removal of a significant fraction of nicotine sorbed

15   to Teflon under both dry and humid air conditions. The effect of ozone was observed as

16   well for cotton under dry air but not at 70% RH. Heterogeneous nicotine-ozone reactions

17   thus depend on the substrate and the presence of co-sorbed water. Additional research

18   is needed to quantify the effect on other materials and at intermediate RH levels.

19   Synthetic carpet, foam cushioning and polyester fabric are hydrophobic indoor materials

20   that are ubiquitous and known to be preferred sorption sites for organic gases (*38*); our

21   initial results suggest that nicotine sorbed to these materials would be subject to ozone

22   oxidation. Indoor RH levels of 20-40% are common and may allow for some

23   heterogeneous ozone-nicotine reactivity even on hydrophilic materials like cotton.

1   One implication of this work is that nicotine sorption models that ignore ozone

2   reaction may substantially overstate nicotine sorptive accumulation over time and thus

3   over-predict inhalation exposures in homes with habitual smoking (*13, 14*).

4   Another important result is that ozone-nicotine reactions yield products of

5   concern to human health and irritancy, notably formaldehyde and N-methylformamide.

6   Thus, ETS-loaded materials can act as long-term sources of secondary pollutants.

7   Production of these secondary pollutants may be magnified by the deliberate use of

8   ozone generators as "air purifiers" to remove ETS components (*39*). The magnitude of

9   secondary pollutant formation in real ETS-contaminated indoor environments and the

10   possibility of heterogeneous reactions between ozone and other sorbing ETS

11   compounds are additional questions deserving of further study.

12

13   **Acknowledgements**

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Figure 4: Stable nicotine oxidation products. Structures indicated with a solid box were positively identified; myosmine (dotted box) was tentatively identified. Suggested reaction pathways were adapted from Tuazon et al (ref. 35).
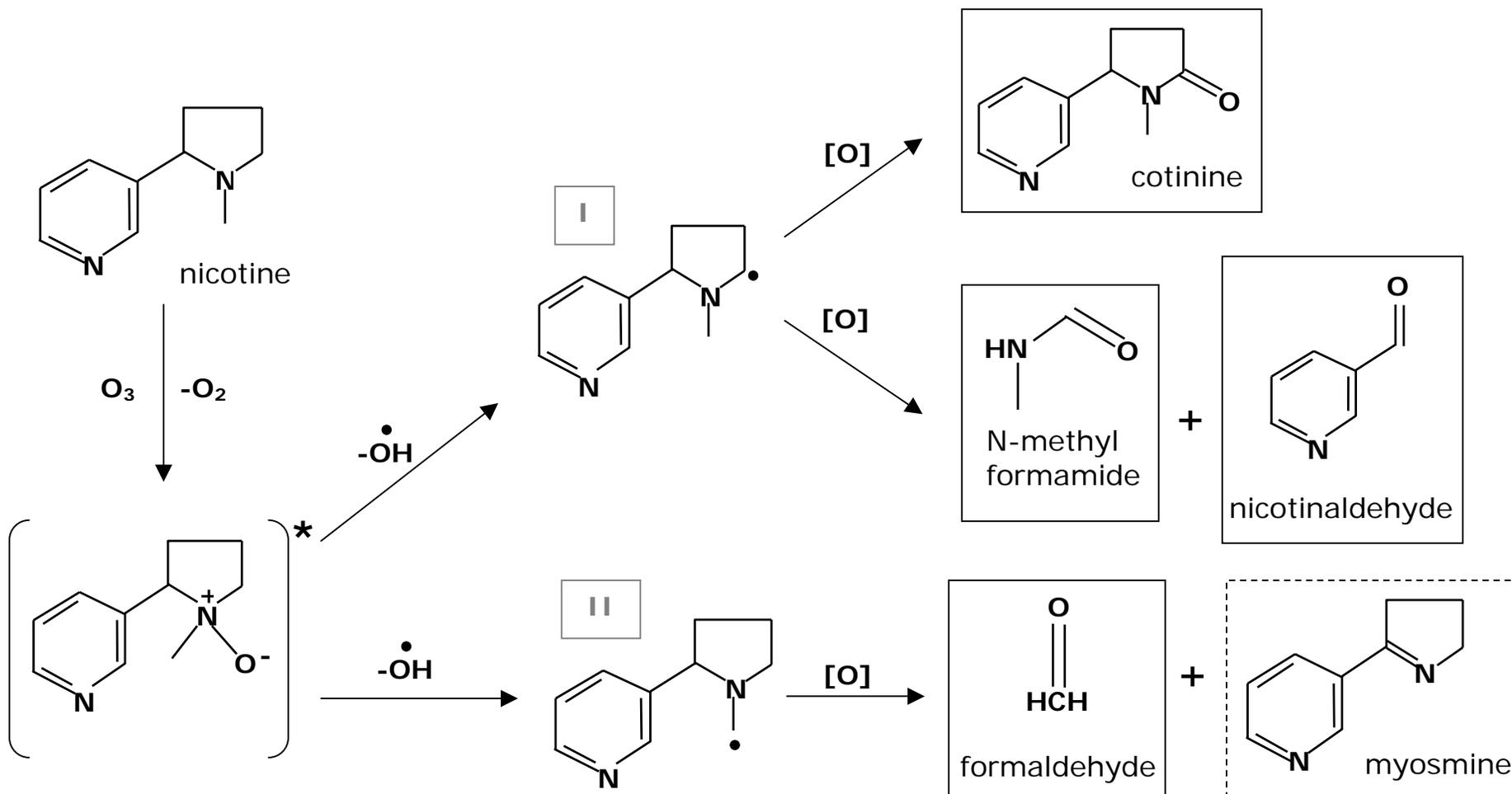
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