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Sublimation Electrification of Organic Compounds

Bijay Banstola and Kermit K. Murray*

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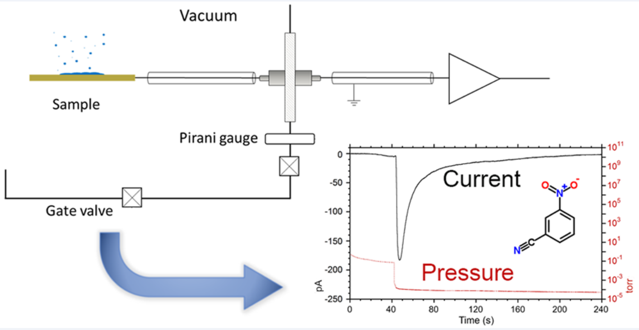
ABSTRACT: The electrification of crystalline deposits of organic compounds under high vacuum was measured and quantified. A group of compounds that produce multiply charged ions by matrix-assisted ionization were deposited on a metal plate, and the current was amplified and recorded; the total charge was obtained by integration of the current. Signals of several hundred picoamperes were obtained within 10 s of the application of high vacuum and persisted for several minutes as the compounds sublimed. The magnitude and sign of the charge were matrix dependent and were affected by the presence of organic or mineral acid in the crystalline deposit, as well as by the application of an electric field. The observations are interpreted as surface electrification caused by the emission of small charged matrix particles during sublimation, with ionic charge carriers comprising protons and hydroxide ions.



■ INTRODUCTION

The formation of ions from solid surfaces for mass spectrometry analysis is influenced by the behavior of charged species at the surface. One important element of surface charging is contact electrification, also known as triboelectric charging, which is the transfer of charge between solid surfaces that are brought into contact and then separated.[1−4] Contact electrification, where at least one of the surfaces is an insulator, can lead to the buildup of static charge and subsequent discharge by spark. These processes are important in industrial applications because electrical discharges can damage solid-state electronics and may cause explosions.[5] On the other hand, contact electrification is employed in many processes, such as electrostatic printing, precipitators, spray coating, and triboelectric generators.[6] The separation of charge in contact electrification can occur through transfer of electrons or ions, material transfer, or bond scission.[3,4,7] Electron transfer is common for metals, but transfer of mobile ions has been postulated as a mechanism for the charging of insulator surfaces.[3] The transfer of nanometer-to-micrometer thickness material, possibly in conjunction with bond breaking and radical formation, has also been suggested as a mechanism for surface charging.[8]

Matrix-assisted ionization (MAI) is a general term used to describe the formation of gas-phase ions from non-volatile compounds that are mixed with a solid or liquid matrix.[9−12] In MAI, the non-volatile molecules are mixed with small molecule matrix compounds, which facilitates formation of highly charged ions. Ion formation can be initiated by physical shock of the crystalline matrix material or phase change by sublimation of solid or boiling of liquid matrix compounds. Physical shock can be provided by a laser pulse[13] or by striking the surface with a mechanical punch,[14] gas pulse,[15] or piezoelectric striker.[16] Ions are produced from solid matrix preparations following the application of a vacuum[17,18] and during the rapid evaporation of liquid matrix mixtures on heated surfaces.[19,20]

The mechanism of MAI is postulated to involve the production of charged particles that generate highly charged ions through the evaporation or sublimation of matrix molecules.[12,21,22] Particle sizing studies indicate that large and small particles are created when MAI solid matrix deposits are mechanically struck.[23] In a recent study, charge from sublimation of MAI matrix compounds was measured using a modified mass spectrometer inlet with an electrically isolated inlet and detector plates.[22] Current pulses of approximately 100 pA and total charge in the nC range were observed for matrix compound particles detected at the inlet and a second detector under vacuum. The current pulses were observed to be coincident with the production of highly charged protein ions in the mass spectrometer. The results were interpreted as the emission of charged particles from the subliming matrix compounds.

In the work described below, the current produced by sublimation of organic compounds was measured using a

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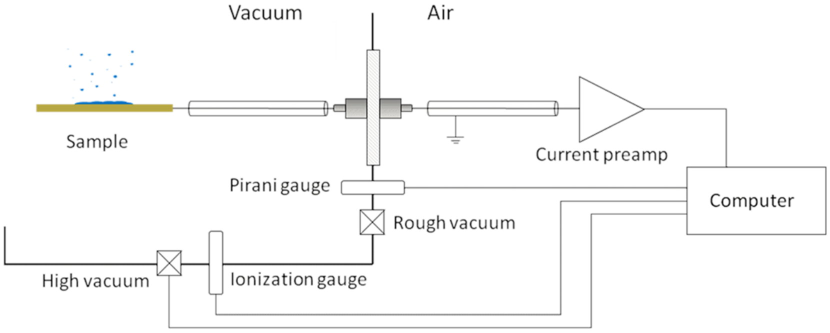

Figure 1. Schematic of the apparatus used for measuring sublimation charge. The sample target is placed in the chamber; rough vacuum is applied, and when the pressure is below 10^{-3} Torr the gate valve is switched manually and the ionization gauge activated. The amplified current, pressure, and gate valve position are digitized and recorded.

device comprising a metal sample plate and current amplifier. Crystalline deposits were formed on the plate by dried droplet deposition from solutions of MAI matrix compounds,[21,22] and the current was measured during the application of high vacuum. The current was integrated to determine the total charge for the compounds under various conditions.

EXPERIMENTAL SECTION

Sublimation was performed in a two-chamber vacuum system comprising two 8 in. conflat six-way crosses separated by a pneumatically actuated gate valve, as shown in Figure 1 and Figure S1. The sample chamber was evacuated with a 3 L/s mechanical vacuum pump with an ultimate pressure of 10^{-2} Torr. The second chamber was evacuated with a 290 L/s turbomolecular pump and was maintained at pressure of 10^{-5} Torr with the gate valve closed. The pressure in the sample chamber was recorded with a Pirani gauge (AGD, Edwards, West Sussex, UK), and the pressure in the high-vacuum chamber was measured with a Bayard-Alpert hot cathode ionization gauge and controller (Model 316, Granville-Phillips, Longmont, CO). A sample plate was constructed from a 25 mm square brass plate with a thickness of 0.5 mm. The plate was attached to a coaxial feedthrough connector and suspended in the center of the sample chamber (Figure S2). The sample plate was connected to a low-noise current-to-voltage pre-amplifier (Oriel Model 70710, Newport, Irvine, CA) set to a gain of 10^9 and 2 ms time constant. The amplified current output was recorded with an analog-to-digital converter (ADC) input of a multifunction I/O device (model 6001, National Instruments, Austin, TX) using software written in LabVIEW (National Instruments).

Matrix samples were deposited on the plate from solution and allowed to dry before the plate was mounted in the sample chamber. Rough vacuum was applied to the sample chamber which achieved a pressure of 10^{-1} Torr after approximately 80 s at which time the gate valve was opened. The pressure reached 10^{-3} Torr after the gate valve was opened, then decreased below 10^{-4} Torr within 5 s and remained constant. Recording of plate current and vacuum (Pirani gauge) was initiated upon application of rough vacuum and continued until the signal returned to baseline, which varied from 3 to 20 min. The plate current was integrated from the time of application of high vacuum to the time at which the signal decayed to 5% of the maximum to yield the total charge produced in a sublimation experiment. Heating of the plate was accomplished using a thermostatically controlled flexible polyimide resistance heater (KHLV, Omega, Norwalk, CT) attached to the bottom of the plate current supplied using a power feedthrough. The temperature was measured with a thermocouple attached to the top of the sample plate.

Scanning electron microscope images (Quanta 3D FEG, FEI, Hillsboro, OR) were obtained from aluminum plates placed 3 mm from the sample plate either above (sample facing up) or below (sample facing down). In some cases, the SEM plates were coated with a thin film of Formvar (SPI Supplies, West Chester, PA) to aid in material collection. The plates were coated with a layer of sputtered gold prior to SEM analysis.

Crystalline deposits were made by depositing solutions of the compounds 2-nitrobenzonitrile (2-NBN), 3-nitrobenzonitrile (3-NBN), 2-nitrophloroglucinol (2-NPG), 1,2-dicyanobenzene (1,2-DCB), 2,5-dihydroxyacetophenone (2,5-DHAP), 2-naphthol, coumarin, anthracene, and carbazole (Sigma-Aldrich, St. Louis, MO). Acetone, trifluoroacetic acid (99%; TFA), formic acid (FA), hydrochloric acid (38%; HCl), and acetonitrile (ACN) were used as received (ThermoFisher Scientific, Waltham, MA, USA). Solutions were prepared by dissolving 10 mg of each compound in 100 μL of ACN with the exception of carbazole which was dissolved in 100 μL acetone. The compound 2,5-DHAP is only partially soluble in ACN therefore a saturated solution of 2,5-DHAP in 1:1 (v/v) ACN and ethanol was used.

RESULTS AND DISCUSSION

A set of nine MAI matrix compounds were selected for this study. A thin film of the compound was formed by depositing a solution on the plate and air drying. The current produced during sublimation was measured under various conditions.

The current recorded during the sublimation of 3-NBN from a deposit of 500 μg as a function of time after vacuum was applied to the sample chamber is shown in Figure 2. The current recorded is negative, indicating that net positive charge is leaving the plate on sublimation. The pressure in the chamber was approximately 0.1 Torr under rough vacuum on and the current produced was less than pA. The gate valve was opened at 52 s and the pressure decreased within 5 s to 10^{-4} Torr, the lower limit of the Pirani gauge. During sublimation, the pressure recorded by the Bayard-Alpert gauge was approximately 10^{-5} Torr. The current increased to its maximum of 180 pA within 5 s and returned to baseline with an exponential decay 1/e time constant of approximately 50 s. There was no matrix material visible on the plate after the system was returned to atmospheric pressure. The charge produced by sublimation of 3-NBN was obtained by

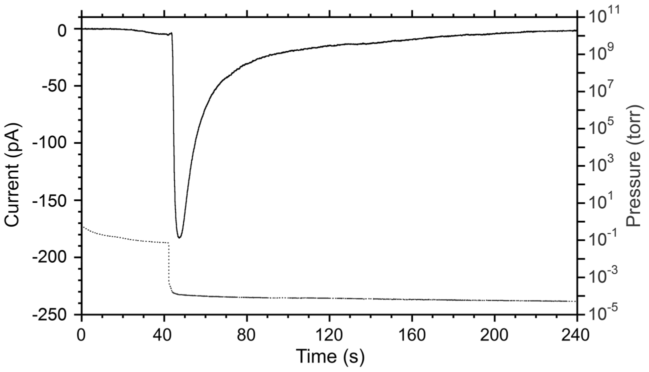

Figure 2. Current recorded during the sublimation of 3-NBN (solid line) and pressure inside the chamber (dotted line).

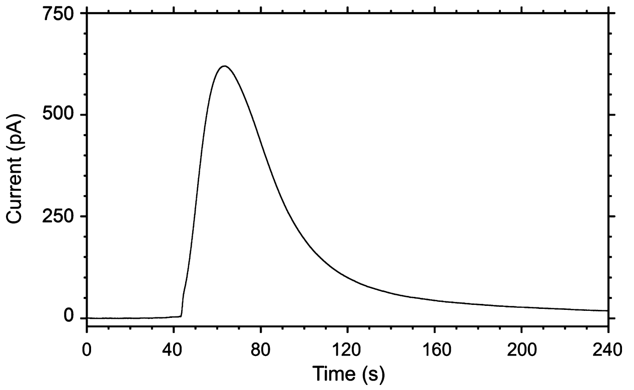

Figure 3. Current recorded during the sublimation of 2-NBN; high vacuum was applied at 40 s.

integrating the current from the time of opening of the gate valve to time at which the signal returned to 5% of the baseline. The net charge produced by sublimation of the 500 μg of 3-NBN was 3.4 nC with an error of 0.5 nC obtained from three replicates (Table 1).

The current produced from sublimation of a 500 μg deposit of 2-NBN is shown in Figure 3. The current flow is the opposite of that for 3-NBN indicating that the net charge leaving the plate is negative. The rise to maximum current is slower than 2-NBN, requiring 20 s to reach maximum and returning to baseline with a decay constant of approximately 120 s. The current obtained from sublimation of 1,2-DCB, coumarin, and 2-NPG is shown in Figure S3 and is tabulated with the other compounds tested in Table 1. The compound 1,2-DCB produced 9.1 nC, coumarin produced 1.4 nC, and 2-NPG produced 0.45 nC net negative charge recorded when a 500 μg deposit of each matrix was sublimed. The compounds 2,5-DHAP, carbazole, 2-naphthol, and anthracene did not produce current above the detection limit.

The charge produced as a function of sample deposit area was measured for 3-NBN with spots 0.5, 1, and 2 cm in diameter made from solutions containing 0.5 mg of 3-NBN. The integrated charge recorded was 3.5 ± 0.2, 5.1 ± 0.3, and 10.7 ± 0.5 nC, corresponding to 1100, 400, and 200 elementary charges per square micrometer deposit. The quantity of charge produced per unit area is comparable to that observed for electrification of insulating materials and is on the order of 100−1000 charges per square micrometer.[1,2] The signal obtained from a typical crystalline deposit was approximately twice that of comparable quantity of matrix powder, suggesting that the surface morphology is also important in addition to surface area.

The effect of sample temperature was investigated using thermostatic heating of the target plate for the matrices 2-NBN and 3-NBN. Heating from room temperature (ca. 21 °C) to 30 °C was initiated when rough vacuum was applied and the plate reached the set temperature within 30 s. At this temperature, the current peaks were approximately one-third narrower and the magnitude of the charge lower by a factor of 3, likely due to the rapid sublimation of the compounds at the higher temperature. No current was detected at 40 °C. The matrices 2-naphthol, anthracene, carbazole, and 2,5-DHAP did not produce current when heated. All of the matrices sublimed from the plate except 2,5-DHAP which remained on the plate even after heating. In general, the target heating results were inconsistent due to the rapid sublimation of the compounds.

The effect of solution acidity was tested with the acids TFA, FA and HCl that were added to the matrix solution before deposition. The charge obtained for 2-NBN and 3-NBN as a function of TFA mass percentage (mass of TFA relative to the solid matrix) is shown in Figure 4. With no added TFA, 2-NBN results in 13 nC net positive charge detected (corresponding to negative charge emitted) and this charge decreases to zero with added acid. With no added TFA, 3-NBN recorded 2 nC negative charge which corresponds to emission of net positive charge. The emission of net positive charge increased to 10 nC at 0.6% TFA then decreased at higher percentage acid. The effect of decreasing net negative charge detected and positive charge emitted with increasing mass percentage acid was also observed for FA and HCl. With

Table 1. Compounds with Current and Net Charge Measured on Sublimation

			charge (nC)			
compound	maximum current (pA)	time to maximum (s)[a]	low vacuum	high vacuum	charge per molecule	decay time (s)[b]
3-NBN	−180	5	−0.03	−3.4	1×10^{-8}	110
2-NBN	620	20	<0.01	16	5×10^{-8}	120
1,2-DCB	160	20	<0.01	9.1	2.4×10^{-8}	170
coumarin	240	5	0.2	1.4	0.4×10^{-8}	10
2-NPG	10	5	<0.01	0.45	0.2×10^{-8}	180
2-naphthol	<1	NA	<0.01	<0.01	NA	NA
carbazole	<1	NA	<0.01	<0.01	NA	NA
anthracene	<1	NA	<0.01	<0.01	NA	NA
2,5-DHAP	<1	NA	<0.01	<0.01	NA	NA

[a]Time to current maximum after high vacuum applied. [b]Time from maximum to 5% of the maximum.

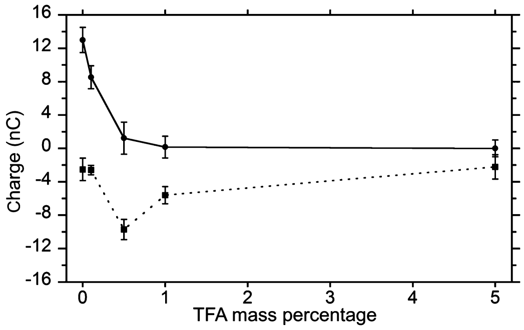

Figure 4. Charge recorded from sublimation of 2-NBN (solid line) and 3-NBN (dotted line) as a function of trifluoroacetic acid mass percentage.

2-NBN, the negative charge emission decreased from 13 nC with no acid to zero at 6% FA or HCl (Figure S4). For 3-NBN and FA, the emission of positive charge was 2 nC with no acid and increased to more than 6 nC at 12% FA (Figure S5). For 3-NBN and HCl, the emission of positive charge decreased slightly from 2 nC to near zero with the addition of acid.

A metal plate identical in size to the sample plate was placed at a 3 mm distance from the sample plate and a static potential was applied to test the effect of electric field on sublimation electrification. A schematic of the system configuration is shown in Figure S6. The net charge produced on sublimation of 0.5 g deposits of 2-NBN and 3-NBN at potentials 0, ±50, and ±100 V are shown in Figure 5. The net charge recorded for 2-NBN corresponds to emitted negative charge and increases from 13 to 25 nC when a positive voltage is applied and decreases to zero at −50 V and to a net 3 nC negative charge recorded that corresponds to positive charge emitted at −100 V. The 3-NBN emits a net 3 nC positive charge with no voltage which increases to 5 nC positive charge at −100 V and emits 6 nC negative charge at +100 V when the polarity is reversed.

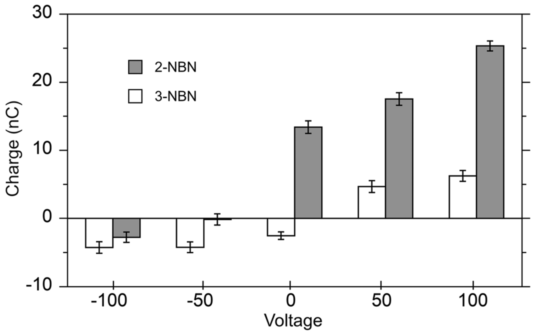

Figure 5. Net charge recorded from sublimation of 2-NBN and 3-NBN as a function of voltage applied to a plate separated by 3 mm from the subliming material.

The current from sublimed material was measured using the second plate at a distance of 3 mm from the sublimation plate (Figure S7). The current on the plate was measured after application of rough vacuum and the net charge was found by integration of the current as described above. The current found for 3-NBN and 2-NBN was approximately half of that recorded for emission from the corresponding compound by sublimation. The charge detected for 3-NBN was positive and for 2-NBN it was negative. An attempt was made to collect sublimed material on aluminum and Formvar-coated aluminum; however, SEM images did not show any particulate or other material.

The results above demonstrate sublimation electrification from deposits of 3-NBN, 2-NBN, 1,2-DCB, 2-NPG, and coumarin when exposed to high vacuum below 10^{-4} Torr. The compounds 2-napthol, anthracene, carbazole, and 2,5-DHAP were tested, but did not produce current on sublimation; of these, all sublimed completely within several minutes with the exception of 2,5-DHAP. The recorded electrification charge is positive (emission of negative charge) for all compounds with the exception of 3-NBN for which it is negative (emission of positive charge). For all compounds that produced current, the maximum was observed between 5 and 20 s after the application of high vacuum and decayed with a time constant of two to 3 min with the exception of coumarin, which had a rapid signal drop with a time constant of approximately 10 s. Two compounds, 3-NBN and coumarin, produced low but measurable current under rough vacuum that was less than a tenth that observed under high vacuum. These results suggest that higher instantaneous current signal could be obtained with more rapid reduction in pressure.

In a previous study of MAI matrix electrification, it was found that of 3-NBN, 2-NBN, 1,2-DCB, 2-NPG, and coumarin produced current when the particulate material was introduced into a vacuum inlet of similar design to a mass spectrometer inlet.[22] In this study, the matrix 3-NBN gave the highest signal, whereas in our study the matrix 2-NBN gave the highest signal, but 3-NBN was unique in emitting net positive charge. Carbazole and anthracene, which did not produce sublimation electrification in our study, required high inlet tube temperatures to produce charge in the previous study: all of the compounds produced negative current at the transfer capillary and positive current at the detector, with the exception of coumarin, which produced positive current at the capillary and negative current at the detector.[22] As in our study, the sign and magnitude of the current was dependent on the compound and conditions.

The above results can be interpreted in terms of a contact electrification mechanism in which charged particles are emitted from the surface as the crystalline matrix material sublimes.[22] Crystal cracking, electrification, and charged particle ejection may be due to bubbles of gas formed by the subliming material or residual solvent within the crystals causing stress and fracturing.[18] The addition of acid to the deposit has the effect of increasing the quantity of net positive charge emitted, which suggests that the charge carriers are H^+ and OH^- ions and the electrification of the particles as they leave the surface is due to the balance between the number of adsorbed OH^- and solvated H^+ at the surface. The charge detected is the net charge and therefore the total charge of either sign is likely much larger than that recorded on sublimation. It has been postulated that contact electrification can proceed through the redistribution of hydroxide ions adsorbed on surfaces that come into contact and then separated.[3] In this hydroxide adsorption model, the H^+ ions are solvated whereas the OH^- ions are localized in the Stern layer and are transferred from one surface to the other through a water bridge when the surfaces come into contact.[24] Separation of the surfaces results in separation of charge. In the MAI case, the water of the water bridge may be residual solvent in the crystal or water at the crystal surface.

CONCLUSIONS

We have measured and quantified the current generated by sublimation of organic compounds that are known matrix compounds for matrix-assisted ionization. The current flow indicates the emission of net negative charge for all compounds tested, with the exception of 3-NBN which emitted a net positive charge. The integrated current is typically between 1 and 10 nC for 1 cm diameter spots ,which corresponds to approximately 100−1000 elementary charges per μm^2. Organic and mineral acids added to the matrix solution prior to deposition increased the quantity of positive charge emitted on sublimation. A conducting plate placed 3 mm above the subliming material and held at a potential of several hundred volts influenced the sign of the charge emitted. When the amplifier was connected to the conducting plate above the subliming material, current was detected with current flow corresponding to negative surface emission, with the exception of 3-NBN.

The sublimation electrification of the matrix materials is consistent with the postulated mechanism of MAI under vacuum, in which the subliming matrix or trapped gas results in crystal fracture upon the application of vacuum.[22] Small particles created in the fracturing process are ejected from the sample, and matrix evaporation or further fracturing results in the formation of highly charged ions that can be detected by mass spectrometry. Measurement of charge emitted as reported above suggests that these particles are charged by electrification, which is limited by the dielectric breakdown of the gaseous subliming matrix. The charge carriers appear to be H^+ and OH^-, the latter possibly adsorbed on the matrix crystals. Particles were not detected in our study, but this is most likely due to the sublimation of the material during collection for analysis. The ability to detect both positive and negative charges by the application of an electric field suggests that both are emitted on sublimation and that the charge detected represents the net charge emitted.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jasms.9b00124.

> Figure S1: Photograph of sublimation chamber. Figure S2: Sublimation sample target and coaxial connection photograph. Figure S3. Current from sublimation of 1,2-DCB, coumarin and 2-NPG. Figure S4: Charge detected from sublimation of 2-NBN as a function of FA and HCl concentration. Figure S5: Charge detected from sublimation of 3-NBN as a function of FA and HCl concentration. Figure S6: Schematic of sublimation current measurement apparatus with second plate for voltage application. Figure S7: Schematic of sublimation current measurement apparatus with second plate for detection of emitted charge. (PDF)

AUTHOR INFORMATION

Corresponding Author

Kermit K. Murray − *Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana 70803, United States;* orcid.org/0000-0002-4976-2263; Phone: +1 (225) 578-3417; Email: kkmurray@lsu.edu; Fax: +1 (225) 578 3458

Author

Bijay Banstola − *Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana 70803, United States*

Complete contact information is available at: https://pubs.acs.org/10.1021/jasms.9b00124

Notes

The authors declare no competing financial interest.

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